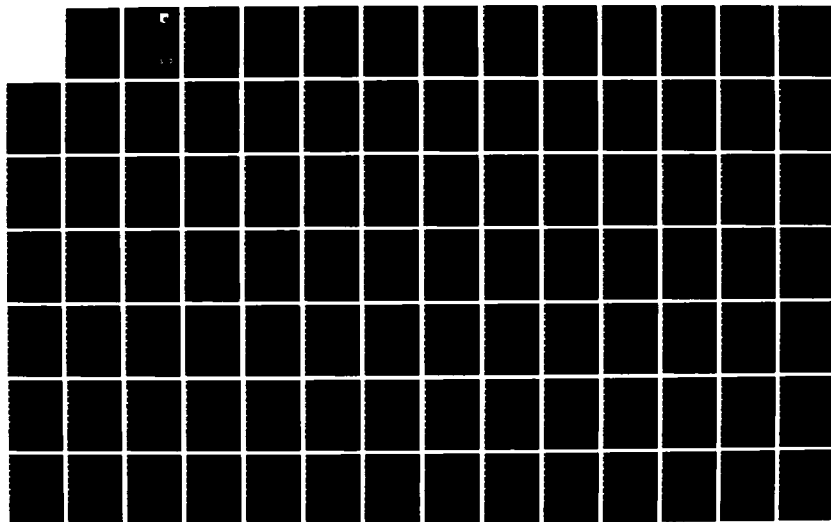AD-A140 486   CLUSTER CALCULATION OF ELECTRONIC STRUCTURE OF THE   1/2
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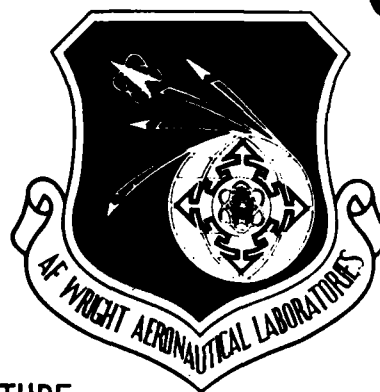UNCLASSIFIED DEC 83 AFWAL-TR-83-1130   F/G 12/1   NL

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CLUSTER CALCULATION OF ELECTRONIC STRUCTURE
OF THE DIAMOND (111) SURFACE USING THE
Xα-SCATTERED WAVE METHOD

William T. McKeown

Electro-Optics Technology Branch
Electronic Technology Division

December 1983

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This report describes a computer-based calculation of the energy eigenvalues of electrons in the C_5H_9 diamond-structural complex, which serves as a cluster model of the diamond (111) surface. The computer-generated calculations are based on the self-consistent-field scattered wave + x-alpha method initially pioneered in the work of John Slater and later developed by Keith Johnson and coworkers at M.I.T.

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The report discusses the theoretical aspects of (1) Hartree-Fock Theory; (2) Self-Consistent-Field Theory and (3) Scattering Theory. It also contains a discussion on the computer programs in a broad context, highlighting the general approach taken.

Lastly, it discusses the calculated results for C_5H_9 and compares these with earlier work of others obtained using the same computational scheme applied to the C_5H_{12} cluster as a model of crystalline diamond.

The results are also compared with a published pseudopotential calculation of the diamond (111) surface which does not use a cluster approach. Good agreement with these calculations and with experiment is obtained for the energy gap in diamond. In addition the location and energy spread of the surface states which appear in the gap agree well with the pseudopotential calculation. The cluster method used thus appears promising for modeling surfaces and localized defects in covalently bonded solids having the diamond structure.

PREFACE

The primary purpose of this report is to provide the reader with enough background in scattering theory and other disciplines to enable him to better understand what is involved in calculations of the energy eigenvalues of electrons in a cluster model. This report discusses Hartree-Fock equations, self-consistent field theory, and scattering theory.

The author supplemented the presentation with derivations which are ordinarily left out of journal articles. Although not an easy task, the author consolidated material from many references in a moderately successful manner. The author wishes to acknowledge all of the authors cited in the reference section, particularly K. H. Johnson whose material Section IX was based upon.

The author wishes to thank Dr. Gust Bambakidis for helping him to run the required computer programs. Without his help, the computations could not have been made. He also wishes to express appreciation to Dr. Bambakidis for suggesting this report topic as well as for providing him with new insights into a complex physical problem. The author wishes to thank Dr. Donn Shankland of the Air Force Institute of Technology (AFIT). Over the course of attending his lectures on Quantum Mechanics and Its Formalism, he became exposed to Green's Functions and other concepts which provided the necessary tools for the theory contained in this report.

Finally, the author wishes to express his sincerest thanks to Mr. Frank R. Kile, Jr. for providing his artistic talents to this project. Frank drew all the figures in the text in the most professional fashion.

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SECTION I

INTRODUCTION

This report describes a computer-based calculation of the diamond structured complexes, C_5H_9 and C_5H_{12}. It results in a calculation of the energy eigenvalues of electrons in these two molecular complexes. The computer programs are based on the self-consistent-field scattered wave + X-alpha (SCF-SW+Xα) method, a concept originally fathered by John C. Slater and later developed by Keith Johnson and co-workers at M.I.T.

The report is divided into three parts (1) theoretical aspects, (2) discussion of the programs, and (3) discussion of the results.

The main thrust of the report is not the calculation itself, but the development of the theoretical background engendered in the calculation. The author preferred this approach because the theoretical background is not readily at hand, but, on the contrary, scattered about an incoherent fashion in the literature. The inception of X-α scattered wave theory began in 1937. It finally reached a degree of maturity in the late sixties. Much work has been done on the subject, and many disciplines enter into the fabric of the topic: Hartree-Fock theory, numerical methods, quantum mechanics, quantum statistical mechanics, theory of solids, group theory, and mathematical physics are all interwined.

It is the author's desire that this report provide some degree of coherency to the topic as well as insight into the true complexity of the problem.

SECTION II

INTUITIVE DESCRIPTION OF THE SELF-CONSISTENT APPROACH
TO THE ELECTRONIC STRUCTURE OF ATOMS

D. R. Hartree devised the self-consistent-field method in 1928.
Essentially, he assumed that each electron moves in an averaged potential
arising from the other electrons in an atomic system. The Schrödinger
equation for an electron moving in that potential is then solved; this
is a relatively simple problem since spherical symmetry is assumed.

The wave function with the desired quantum number in that potential
is then selected. This wave function Ψ is then assumed to be used in
finding the charge density arising from that particular electron in
question. The total charge density arising from all the electrons
present in the atom is built up. The potential arising from this charge
density (solution of Poisson's equation) is calculated by electrostatics,
and then the requirement for self-consistency is made, that is, this
final potential must agree with the initial one which had been assumed
in setting up Schrödinger's equation.

Reiterating, Hartree found that he could set up a very manageable
procedure for determining the self-consistent field, based on a method
of iteration or successive approximation. He started by assuming trial
wave functions, which he hoped were nearly the final ones. From these
functions he determined charge densities and potentials, and solved the
Schrödinger's equation, coming out with final wave functions. Since he
could not have expected to have achieved self-consistency, these final
wave functions would not agree with the initial ones. But then he started
a new cycle of operation using the final functions of one step as the
starting functions of the next step, finding charge densities, potentials,
and so on, from them and proceeding just as before. Fortunately, he
found that this process converged by carrying through a number of cycles;
he came out with the wave functions which were self-consistent to a very
good approximation.

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SECTION III

THE HARTREE SELF-CONSISTENT-FIELD METHOD

In the Hartree Method, it is assumed that each electron moves in a
central field, produced by a nucleus and the spherically-averaged potential
fields of every other electron.

We assume, first of all, that the one-electron wave functions or
orbitals, as we shall call them, have the form

$$U_{n\ell m_\ell}(r,\theta,\phi) = (-1)^{(m_\ell+|m_\ell|)/2} \sqrt{\frac{(2\ell+1)(\ell-|m_\ell|)!}{(\ell+|m_\ell|!)}}$$

$$\times R_{n\ell}(r) \, P_\ell^{|m_\ell|}(\cos\theta) \, \exp(im_\ell\phi),$$

where the substitution

$$P_{n\ell}(r) \equiv r R_{n\ell}(r)$$

will be made, with $R_{n\ell}$ or $P_{n\ell}$ normalized so that

$$\int_0^\infty [P_{n\ell}(r)]^2 dr = 1$$

The function $P_\ell^{|m_\ell|}(-\cos\theta)$ is the associated Legendre polynomial.

Next, we inquire how a wave function for the N-electron atom can
be constructed out of these one-electron orbitals. Each electron is
supposed to move quite independently of the others, being acted on by
the others only in an averaged manner. This implies that the wave
function ψ should be a product of functions of the various electrons or:

$$-\psi(r,\theta,\phi\ldots r_N\theta_N\phi_N) = U_{n_1\ell_1 m_1}(r,\theta,\phi)\ldots U_{n_N\ell_N m_{\ell_N}}(R_N,\theta_N,\phi_N) \tag{1}$$

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where the U's on the RHS of Equation 1 are the orbitals, each one a function of the coordinates of a single electron. We assign the quantum numbers, n,ℓ,m_ℓ, etc. for the various electrons according to the configurations in which we expect the atom to be found.

Equation 1 does not represent an exact solution of Schrödinger's equation for the atom; it is an approximate function containing the undetermined radial functions $R_{n_{N\ell N}}(r)$ as quantities may be varied. For this reason, we can carry through this as a variational problem, and the wave functions prove to be very nearly those of Hartree's method. If we slightly modify the calculation, we get Hartree's equation. We then modify it by not exactly computing the average energy, but by making the spherical average of the potential of an electron which underlies Hartree's approximation.

1. EXPECTATION VALUE OF THE ATOMIC HAMILTONIAN

The first step in applying the variation method to Hartree's wave function is to compute the average value of the Hamiltonian for the wave function of Equation 1 making the approximation of spherical averaging. The Hamiltonian for an N-electron system is

$$(H)_{op} = -\Sigma(i)\nabla_i^2 - \Sigma(i)\frac{2z}{r_i} + \Sigma(\text{pairs } i,j)\frac{2}{r_{ij}} \tag{2}$$

where the summation over i is also over all N electrons, that summation over pairs is over each pair counted once, excluding the case $i=j$. The first term in Equation 2 is the sum of the kinetic energies of all electrons, the second is the potential energy in the field of the nucleus, r_i being the distance from the nucleus to the ith electron, and the last is the repulsive Coulomb potential of interaction between the ith and jth electrons. We understand that we are to perform a spherical average of this repulsive interaction. Equation 2 is in atomic units. It is convenient to rewrite Equation 2 as:

$$(H)_{op} = \Sigma(i)f_i + \Sigma(\text{pairs } i,j) g_{ij} \tag{3}$$

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where

$$f_i = -\nabla_i^2 - \frac{2z}{r_i}; \quad g_{ij} = \frac{2}{r_{ij}}$$

We now let the operator of Equations 2 or 3 operate on the wave function, multiply by the conjugate of the wave function, and integrate over all values of the coordinates.

First, we will look at the operator f_i

$$\int U^*_{n_i \ell_i m_{\ell_i}} (r_i, \theta_i, \emptyset_i) f_i \, U_{n_i \ell_i \, m_{\ell_i}} (r_i \theta_i \emptyset_i) \, dv_i = (i|f|i) \tag{4}$$

Next, we will consider one of the two-electron operations g_{ij}. It operates on two orbitals with indices i and j. We can then integrate over the coordinates of all electrons except these two and find as the contribution of this operation g_{ij} to the average Hamiltonian

$$\iint \left[U^*_{n_i \ell_i m_{\ell_i}} \, U^*_{n_j \ell_j m_{\ell_j}} \, g_{ij} \, U_{n_i \ell_i m_{\ell_i}} \, U_{n_j \ell_j m_{\ell_j}} \right]_{average} dv_i \, dv_g \tag{5}$$

$$= (ij|g|ij)av$$

We can now combine these results, and find that

$$(H)av = \Sigma(i) \, (i|f|i) + \Sigma(pairs \; i,j) \, (ij|g|ij) \; av \tag{6}$$

2. ENERGY INTEGRALS FOR THE HARTREE CALCULATION

We know

$$-\nabla u^2 = \frac{(-1)^{(m_\ell + |m_\ell|)/2}}{\sqrt{4\pi}} \sqrt{\frac{(2\ell+1)(\ell-|m_\ell|)!}{(\ell+|m_\ell|)!}}$$

$$\times P_\ell^{|m_\ell|} (\cos\theta) \exp(im_\ell \emptyset) \frac{1}{r} \left[-\frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{r^2} \right] P_{n\ell}(r) \tag{7}$$

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where u, n, ℓ, M_ℓ, r, θ, ϕ stand for U_i, ℓ_i, etc. if we are dealing with
the function u_i. We multiply by U_i^* and integrate over coordinates,
making use of the properties of the associated Legendre functions. We
find:

$$\int U_{n_i \ell_i m_{\ell_i}}^* (-\nabla_i^2) U_{n_i \ell_i m_{\ell_i}} \, dv_i = \int_0^\infty P_{n_i \ell_i}(r_i) \left[-\frac{d^2}{dr_i^2} + \frac{\ell_i(\ell_i+1)}{r_i^2} \right]$$
$$\times P n_i \ell_i \, dr_i \tag{8}$$

As for the term $-\frac{2z}{r_i}$ in the operator f_i, we can carry out immediately
the integration over angles which leaves a radial integration only.
Hence, we arrive at

$$(i|f|i) = \int_0^\infty P_{n_i \ell_i}(r_i) \left[-\frac{d^2}{dr_i^2} + \frac{\ell_i(\ell_i+1)}{r_i^2} - \frac{2z}{r_i} \right] P_{n_i \ell_i}(r_i) dr_i \tag{9}$$

We shall denote this one-electron integral as

$$(i|f|i) = I(n_i \ell_i) \tag{10}$$

Next, we consider the two-electron integral of Equation 5. This represents
the Coulomb interaction energy between a charge distribution $U_{n_i \ell_i m_{\ell_i}}^*$
$(r_i \theta_i \phi_i)$ $U_{n_i \ell_i m_{\ell_i}} (r_i \theta_i \phi_i)$ and another charge distribution $U_{n_j \ell_j m_{\ell_j}}^*$
$(r_j \theta_j \phi_j) U_{n_j \ell_j m_{\ell_j}} (r_j \theta_j \phi_j)$ where it is understood that we are to perform
a spherical average of the charges or potentials. To do the integral,
we can first compute the quantity

$$U_{n_j \ell_j m_{\ell_j}}^* (r_j \theta_j \phi_j) U_{n_j \ell_j m_{\ell_j}} (r_j \theta_j \phi_j) \left(\frac{2}{r_{ij}} \right) dv_j \tag{11}$$

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This is the electrostatic potential energy (in atomic units) of the charge distribution of the jth electron, at the position of the ith. Then, we multiply this by the charge distribution $U^*_{n_i \ell_i m_{\ell_i}}(r_i \theta_i \phi_i)$

$U_{n_i \ell_i m_{\ell_i}}(r_i \theta_i \phi_i)$ of the ith electron and integrate over dv_i. This is exactly what Equation 4 says.

In addtion to this, we must perform a spherical average. We must take the total charge enclosed in a spherical shell bounded by spheres of radii r_j, $r_j + dr_j$, and replace the actual charge by a charge distribution in which this same charge is uniformly distributed through the shell. Now the charge located in the volume bounded by r_j, $r_j + dr_j$, θ_j, $\theta_j + d\theta_j$, ϕ_j, $\phi_j + d\phi_j$ is the volume element $r_j^2 \sin \theta_j dr_j d\phi_j$ times the product of the wave function and its conjugate. Hence, the charge located in the spherical shell will be the integral of this quantity over θ and ϕ or

$$\frac{1}{4\pi} \frac{(2\ell_j+1)(\ell_j-|m\ell_j|)!}{(\ell_j+|m_{\ell_j}|)!} P^2_{n_j \ell_j}(r_j)dr_j \int_0^{2\pi} d\phi_j \int_0^{\pi} \left[P_{\ell_j}^{|m_{\ell_j}|}(\cos\theta_j)\right]^2 \sin\theta_j \, d\theta_j \tag{12}$$

times $(-e)$ if we are using ordinary units. The integral over θ_j is given by

$$\frac{2}{2\ell_j+1} \frac{(\ell_j+|m_{\ell_j}|)!}{(\ell_j-|m_{\ell_j}|)!}$$

The integral over ϕ_j is 2π. When we combine these facts, we find that the charge located in the shell between r_j and $r_j + dr_j$ is

$$P^2_{n_j \ell_j}(r_j)dr_j \text{ times } (-e) \tag{13}$$

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In other words, as far as the spherical average is concerned, the result is just as if we had disregarded the functions of angles and used $P^2_{n_j \ell_j}$ directly as the radial charge density.

To find the electrostatic potential of Equation 11, we now wish to find the potential energy of an electron at distance r_i from the origin, in the presence of a shell of radius r_j and of the charge equal to $P^2_{n_j \ell_j}(r_j)dr_j$, using atomic units in which the potential energy of inter-action between two electrons at a distance r is $\frac{2}{r}$. By elementary principles of electrostatics a spherical shell of charge has a potential at external points equal to that of a point charge of the same total charge concentrated at the origin, and at points inside the shell the potential is constant, equal to its value at the surface of the shell. Then the potential energy of the electron at distance r_i from the origin (in the presence of the shell) is

$$\frac{2}{r_i} \; P^3_{n_j \ell_j}(r_j)dr_j \quad \text{if} \quad r_i > r_j \tag{14}$$

$$\frac{2}{r_j} \; P^2_{n_j \ell_j}(r_j)dr_j \quad \text{if} \quad r_i < r_j \tag{15}$$

The total potential energy of the electron at distance r_i from the origin, in the presence of the electron whose wave function is given by $P_{n_j \ell_j}(r_j)$, is then

$$\text{Potential energy} = \frac{2}{r_i} Y_0 \left(n_j \ell_j, \frac{n_j \ell_j}{r_i} \right) \tag{16}$$

where
$$Y_0(n_j \ell_j, n_j \ell_j / r_i) = \int_0^{r_i} P^2_{n_j \ell_j}(r_j)dr_j + \int_{r_i}^{\infty} P^2_{n_j \ell_j}(r_j)\left(\frac{r_i}{r_j}\right)dr_j$$

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The notation $Y_0(n\ell, \frac{n\ell}{r})$ was introduced by Hartree. To evaluate the integral (Equation 5), we must next multiply this potential energy by a spherically averaged charge distribution of the ith electron and integrate over the coordinates of that electron. The result, which we shall designate as $F^°(n_i\ell_i; n_j\ell_j)$, is

$$F^°(n_i\ell_i; n_j\ell_j) = \int_0^\infty P^2_{n_i\ell_i}(r_i)(\frac{2}{r_i})\, Y_0(n_j\ell_j, \frac{n_j\ell_j}{r_i})\, dr_i$$

$$= \int_0^\infty \int_0^\infty P^2_{n_i\ell_i}(r_i)\, P^2_{n_j\ell_j}(r_j)\, \frac{2}{r(B)}\, dr_i dr_j \tag{17}$$

where $r(B)$ is the larger of the two variables r_i, r_j; that is when $r_i > r_j$, $r(B) = r_j$, and when $r_i < r_j$, $r(B) = r_j$.

We now have found the values of the various integrals involved in the average value of the Hamiltonian, and Equation 6 can be rewritten in the form:

$$(H)av = \Sigma(i)I(n_i\ell_i) + \Sigma(\text{pairs } i,j)\, F^°(n_i\ell_i; n_j\ell_j) \tag{18}$$

3. HARTREE EQUATIONS AS DETERMINED BY THE VARIATION METHOD

We are now ready to carry out the variation of the one-electron orbitals so as to minimize the average Hamiltonian of Equation 18. Since we wish to minimize the Hamiltonian with respect to variation of each one of the radial wave functions, we can handle these separately: $(H)av$ must be a minimum as a particular function $P_{n_i\ell_i}$ is varied. The terms of Equation 18 which depend on this function are

$$(H_i)av = I(n_i\ell_i) + (j \neq i)\, F^°(n_i\ell_i; n_j\ell_j) \tag{19}$$

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Let us vary this quantity subject to the condition that the normalization integral $\int_0^\infty P^2_{n_i \ell_i}(r_i)dr_i$ should remain equal to unity. Using Lagrangean multipliers, λ_i such that $\lambda_i = -\varepsilon_{n_i \ell_i}$ where $\varepsilon_{n_i \ell_i}$ is the eigenvalue of the problem. Then

$$\delta(H_i)av - e_{n_i \ell_i} \delta \int_0^\infty P^2_{n_i \ell_i}(r_i)dr_i = 0 \tag{20}$$

then computing the various integrals individually, we have:

$$\delta I(n_i \ell_i) = \int_0^\infty \delta P_{n_i \ell_i} \left[-\frac{d^2}{dr_i^2} + \frac{\ell_i(\ell_{i+1})}{r_i^2} - \frac{2z}{r_i} \right] P_{n_i \ell_i} dr_i$$

$$+ \int_0^\infty P_{n_i \ell_i} \left[-\frac{d^2}{dr_i^2} + \frac{\ell_i(\ell_{i+1})}{r_i^2} - \frac{2z}{r_i} \right] \delta P_{n_i \ell_i} dr_i \tag{21}$$

$$= 2 \int_0^\infty \delta P_{n_i \ell_i} \left[-\frac{d^2}{dr_i^2} + \frac{\ell_i(\ell_{i+1})}{r_i^2} - \frac{2z}{r_i} \right] P_{n_i \ell_i} dr_i$$

where the last equation follows as a result that the integral is real and therefore is equal to its own conjugate. Note also that

$$\int_0^\infty P_{n_i \ell_i} \left(\frac{d^2}{dr_i^2}\right) \delta P_{n_i \ell_i} dr_i = \left(\frac{d}{dr_i} \delta P_{n_i \ell_i}\right) P_{n_i \ell_i} \Big|_0^\infty - \int_0^\infty \frac{d}{dr_i}$$

$$(P_{n_i \ell_i}) \frac{d}{dr_i} \delta P_{n_i \, i} dr_i = \left(\frac{d}{dr_i} \delta P_{n_i \ell_i}\right) P\ell_{n_i \ell_i} \Big|_0^\infty - \frac{d}{dr_i} (P_{n_i \ell_i})$$

$$\delta P_{n_i \ell_i} \Big|_0^\infty + \int_0^\infty \frac{d^2}{dr_i^2} P_{n_i \ell_i} \delta P_{n_i \ell_i} dr_i$$

since the boundary conditions for the extremum at 0 and ∞ are zero and $P_{n_i \ell_i}(r)$ vanishes at 0

and

$$\infty \text{ so } \int_0^\infty P_{n_i \ell_i} \left(\frac{d^2}{dr_i}\right) \delta P_{n_i \ell_i} dr_i = \int_0^\infty \frac{d^2}{dr_i^2} (P_{n_i \ell_i}) \delta P_{n_i \ell_i} dr_i$$

where the minus sign was removed for convenience.

Next, we have

$$\delta F^\circ(n_i \ell_i;\ n_j \ell_j) = 2 \int_0^\infty \int_0^\infty \delta P_{n_i \ell_i}(r_i) P_{n_i \ell_i}(r_i)$$

$$P^2_{n_j \ell_j}(r_j) \frac{2}{r(B)}\ dr_i dr_j$$

$$= 2 \int_0^\infty \delta P_{n_i \ell_i}(r_i)\ P_{n_i \ell_i}(r_i)\ \frac{2}{r_i}\ Y_0\ (n_j \ell_j,\ n_j \ell_j)/r_i)\ dr_i \tag{22}$$

Last we have

$$\delta \int_0^\infty P^2_{n_i \ell_i}\ dr_i = 2 \int_0^\infty \delta P_{n_i \ell_i}\ P_{n_i \ell_i}\ dr_i \tag{23}$$

Then we insert these values into Equation 2, as

$$2 \int_0^\infty \delta P_{n_i \ell_i}(r_i)\ \left[-\frac{d^2}{dr_i^2} + \frac{\ell_i(\ell_{r+1})}{r_i} - \frac{2z}{r_i} \right.$$

$$+ \Sigma(i \neq j)\ \frac{2}{r_i}\ Y_0\ (n_j \ell_j,\ \frac{n_j \ell_j}{r_i})$$

$$\left. - e_{n_i \ell_i} \right]\ P_{n_i \ell_i}\ dr_i = 0 \tag{24}$$

The integral (Equation 24) must be zero for any value of the variation function $P_{n_i \ell_i}(r_i)$ which means that the remaining part of the integrand must be zero. Hence, we have

$$\left[-\frac{d^2}{dr_i^2} + \frac{\ell_i(\ell_{i+1})}{r_i^2} - \frac{2z}{r_i} + \Sigma(j \neq i)\ \frac{2}{r_i}\ Y_0\ (n_j \ell_j;\ \frac{n_j \ell_j}{r_i}) \right] \tag{25}$$

$$P_{n_i \ell_i}(r_i) = e_{n_i \ell_i} P_{n_i \ell_i}(r_i)$$

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Equation 25 is the fundamental equation of the Hartree method.

It is the radial wave equation for an electron moving in a spheri-
cal   potential produced by the nuclear change of z units and by the
spherically average charge distributions of all other electrons. In
other words, we are precisely led to the set of equations which would
be derived from Hartree's original, intuitively derived postulate of the
self-consistent field.

Hartree's equations are of the form called integrodifferential
equations. The only practical method of solving the set of simultaneous
equations for the occupied orbitals is a method of iteration or successive
approximations. As for the actual method used in obtaining the solution
the numerical method will be discussed in detail in a later section.

SECTION IV

FINITE-DIFFERENCE APPROACH TO SCHRÖDINGER'S EQUATION FOR THE SPHERICAL PROBLEM

In the case of spherical symmetry, we can make separation of variables to Schrödinger's equation in spherical coordinates, writing U_i as the product of a function R_i of the radial vector r and a function of $Y_{\ell m}(\theta,\phi)$, where θ and ϕ are the angles in spherical coordinates and ℓ and m are quantum numbers, then

$$\nabla_u^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial u}{\partial r} \right) + \frac{1}{r^2 \sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial u}{\partial \theta} \right)$$

$$+ \frac{1}{r^2 \sin^2\theta} \frac{\partial^2 u}{\partial\phi^2} \tag{26}$$

Substituting $R_i Y_{\ell m}(\theta,\phi)$ for U_i in Equation 26, we have

$$\frac{1}{R_i} \left[\frac{d}{dr} \left(r^2 \frac{dR_i}{dr} \right) + (e_i - v) r^2 R_i \right] = - \frac{1}{Y_{\ell m}} \left[\frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \right.$$

$$\left. \left(\sin\theta \frac{\partial Y_{\ell m}}{\partial \theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2 Y_{\ell m}}{\partial\phi^2} \right] \tag{27}$$

Since the LHS is a function of r only and RHS is a function of θ and ϕ only, each of these is a constant, $\ell(\ell+1)$, so

$$\frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial Y_{\ell m}}{\partial \theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2 Y_{\ell m}}{\partial\phi^2} + \ell(\ell+1)Y_{\ell m} = 0 \tag{28}$$

and

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR_i}{dr} \right) + \left[e_i - V - \frac{\ell(\ell+1)}{r^2} \right] R_i = 0 \tag{29}$$

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The first step in the treatment of Equation 29 is to replace R_i by a function $\frac{P_i}{r}$, so that $P_i = rR_i$, then Equation 29 is converted as follows:

$$\frac{1}{r^2} \cdot 2r \frac{dR_i}{dr} + \frac{d^2R_i}{dr^2} + \left[e_i - V - \frac{\ell(\ell+1)}{r^2}\right] R_i = 0 \tag{30}$$

$$r^2 \frac{d^2R_i}{dr^2} + 2r \frac{dR_i}{dr} + \left[e_i - V\right] r^2 R_i - \ell(\ell+1)R_i = 0 \tag{31}$$

$$R_i = \frac{P_i}{r} \tag{32}$$

$$\frac{dR_i}{dr} = \frac{dP_i}{rdr} - \frac{P_i}{r^2} \tag{33}$$

$$\frac{d^2R_i}{dr^2} = \frac{d^2P_i}{r\,dr^2} - \frac{dP_i}{r^2dr} - \frac{dP_i}{r^2dr} + \frac{2dP_i}{r^3dr} \tag{34}$$

Substituting Equations 33 and 34 into Equation 31, we have:

$$\left(\frac{rd^2P_i}{dr^2} - \frac{2dP_i}{dr} + \frac{2dP_i}{rdr}\right) + 2r\left(\frac{dP_i}{rdr} - \frac{P_i}{r^2}\right) + r[e_i - V]\,P_i - \frac{\ell(\ell+1)}{r}\,P_i = 0 \tag{35}$$

divided by r we have:

$$\frac{d^2P_i}{dr^2} + \left[\epsilon_i - V - \frac{\ell(\ell+1)}{r^2}\right]\,P_i = 0 \tag{36}$$

Letting

$$(11a) \quad g(r) = -\left[e_i - V - \frac{\ell(\ell+1)}{r^2}\right]$$

we have

$$\frac{d^2P_i}{dr^2} = g(r)\,P_i(r) \tag{37}$$

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The most practical way to handle Equation 37 is numerical integration.

1. ITERATIVE SOLUTION PROCEDURE

Suppose we have found values of the function P at a set of equal-spaced values of r, namely, P_{n-2}, P_{n-1}, P_n differing by increments of h of the variable r. Let us suppose we know the expansion of P in power series around the value r_n of r involved in P_n. We then have

$$P_{n\pm1} = P_n \pm hP_n' + \frac{h^2}{2!} P_n'' \pm \frac{h^3}{3!} P_n''' + \frac{h^4}{4!} P_n^{iv} \pm \frac{h^5}{5!} P_n^v + \dots \quad (38)$$

where P_n', P_n'' etc. are successive derivatives of P with respect to r, computed at r_n. We then note that

$$P_{n+1} + P_{n-1} = 2P_n + \frac{2h^2}{2!} P_n'' + \frac{2h^4}{4!} P_n^{iv} + \frac{2h^6}{6!} P_n^{vi} + \dots \quad (39)$$

$$P_{n+1} - 2P_n + P_{n-1} = h^2 P_n'' + \frac{h^4}{12} P_n^{iv} + \dots \quad (40)$$

since

$P_n'' = g_n(r)P_n(r)$. From Equation 37, we have

$$P_{n+1} = (2 + g_n h^2)P_n - P_{n-1} + \frac{h^4}{12} P_n^{iv} + \dots \quad (41)$$

If the intervals of h are small enough so that the fourth order term $\frac{h^4 P_n^{iv}}{12} \sim 0$, this allows us to compute the next entry P_{n+1} in the table if P_n and P_{n-1} are known.

Generally, however, this approximation is not accurate enough. It is therefore customary to use a modification of the procedure suggested by Noumerov, which is more accurate, We define a quantity y_n by the definition:

$$y_n = \frac{P_n - h^2 P_n''}{12} \quad (42)$$

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since

$$y_{n\pm 1} = y_n \pm h y_n' + \frac{h^2}{2} y_n'' \pm \frac{h^3}{6} y_n''' + \frac{h^4}{24} y_n^{iv} + \cdots \qquad (43)$$

$$y_{n\pm 1} = \left\{ P_n - \frac{h^2 P_n''}{12} \right\} \pm h \left(P_n' - \frac{h^2 P_n'''}{12} \right) + \frac{h^2}{2} \left(P_n'' - \frac{h^2 P_n^{iv}}{12} \right)$$

$$\pm \frac{h^3}{6} \left(P_n''' - \frac{h^2 P_n^{v}}{12} \right) + \frac{h^4}{24} \left(P_n^{iv} - \frac{h^2 P_n^{vi}}{12} \right)$$

$$\pm \frac{h^5}{120} \left(P_n^{v} - \frac{P_n^{vii}}{12} \right) + \frac{h^6}{24} \left(P_n^{vi} - \frac{P_n^{viii}}{12} \right) \pm \cdots \qquad (44)$$

$$y_{n\pm 1} = P_n \pm h P_n' + h^2 P_n'' \left(\frac{-1}{12} + \frac{1}{2} \right) \pm h^3 P_n''' \left(\frac{-1}{12} \pm \frac{1}{6} \right) \qquad (45)$$

$$+ h^4 P_n^{iv} \left(\frac{-1}{24} + \frac{1}{24} \right) + h^5 P_n^{v} \left(\frac{\mp 1}{72} \pm \frac{1}{120} \right) + h^6 P_n^{vi} \left(\frac{-1}{(12)(24)} + \frac{1}{24} \right)$$

or

$$y_{n\pm 1} = P_n \pm h P_n' + \frac{5}{12} h^2 P_n'' \pm \frac{h^3}{12} P_n''' \mp \frac{h^5}{180} P_n^{v} - \frac{h^6}{480} P_n^{vi} \cdots \qquad (46)$$

from which

$$y_{n+1} + y_{n-1} = 2 P_n + \frac{5}{6} h^2 P_n'' - \frac{h^6}{240} P_n^{vi} \qquad (47)$$

or for

$$P_n = y_n + \frac{h^2 P_n''}{12}$$

we have

$$y_{n+1} - 2 y_n + 2 y_{n-1} = h^2 P_n'' - \frac{h^6}{240} P_n^{vi} \cdots \qquad (48)$$

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showing that the fourth term has disappeared. Using $\dfrac{d^2 P_i}{2} = g(r) \, P_i(r)_2$,
we may rewrite $y_n = P_n - \dfrac{h^2 P_n''}{12}$ as $y_n = P_n - \dfrac{h^2}{12} g_n P_n = P_n\left(1 - \dfrac{h^2}{12} g_n\right)$.

$$y_{n+1} = 2y_n - y_{n-1} + h^2 \left[\frac{12P_n - 12y_n}{h^2}\right] - \frac{h^6}{240} P_n^{vi} \tag{49}$$

$$y_{n+1} = 2y_n - y_{n-1} + \left[\frac{12 \cdot y_n}{\dfrac{1 - g_n h^2}{12}} - 12y_n\right] - \frac{h^6}{240} P_n^{vi} \tag{50}$$

or

$$y_{n+1} = \left(2 + \frac{g_n h^2}{\dfrac{1 - g_n h^2}{12}}\right) y_n - y_{n-1} - \frac{h^6}{240} P_n^{vi} \tag{51}$$

Here the sixth-order term is small enough to neglect in actual cases, so Equation 51 is used to carry out the Noumerov integration. First, this is done by constructing a table of values of the quantities $\dfrac{g_h h^2}{12}$ from equation $g(r) = -\left[e_i - v - \dfrac{\ell(\ell+1)}{r^2}\right]$. Then, we carry through two columns, one of y_n, the other of P_n. From the entries in the y_n table, up to y_n itself, we can use Equation 51 to find $y_n + 1$ and from equation $y_n = P_n\left\{1 - \dfrac{g_n h^2}{12}\right\}$ we get P_{n+1}.

The iterative procedure has been followed in the succeeding software program.

Once P_n, P_{n-1} and P_{n+1} has been calculated, then Simpson's rule can be employed to calculate the integral. This is proven as follows:

$$\text{Since } P = P_n + (r-r_n) P_n' + \frac{(r-r_n)^2}{2} P_n'' + \cdots \tag{52}$$

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then

$$\int_{r_n-h}^{r_n+h} P dr = \int_{r_n-h}^{r_n+h} \left[P_n + (r-r_n) P_n' + \frac{(r-r_n)^2}{2} P_n'' \right] dr$$

$$= P_n \, 2h + \frac{2h^3}{6} P_n'' + \cdots \approx 2h \left[P_n + \frac{h^2}{6} P_n'' + \cdots \right] \tag{53}$$

since $h^2 P_n'' = P_{n+1} - 2P_n + P_{n-1}$, then we find

$$\int_{r_n-h}^{r_n+h} P dr = 2h \left[P_n + \frac{P_{n+1}}{6} - \frac{1}{3} P_n + \frac{P_{n-1}}{6} + \cdots \right] \tag{54}$$

$$= \frac{h}{3} \left| P_{n-1} + 4P_n + P_{n+1} \right|$$

Equation 54 is a simple form of Simpson's rule; instead

$$\int_{r_n-h}^{r_n+h} P dr \rightarrow \int_{r_n-h}^{r_n+h} P^2 dr \text{ which can be employed to} \rightarrow \int_0^\infty p^2 dr = N \text{ normalizing,}$$

we have

$$\int_0^\infty \left[\frac{P}{\sqrt{N}} \right]^2 dr = 1 \text{ so Simpson's rule can be used to find definite}$$

integrals or indefinite integrals up to a given entry in the table and its procedure is followed to find the normalization factors for the radial wave function.

(Quadratic integrands do not follow Simpson's rule. This is shown as follows.

$$\text{for } \int_{r_n-h}^{r_n+h} p^2 dr$$

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$$P^2 = \left[P_n + (r-r_n)P_n^i + \frac{(r-r_n)^2}{2} P_n^{ii} + \cdots \right]\left[P_n + (r-r_n)P_n^i \right.$$

$$\left. + \frac{(r-r_n)^2}{2} P_n^{ii} \right]$$

$$= P_n^2 + 2P_n(r-r_n)P_n^i + \frac{2(r-r_n)^2}{2} P_n^{ii}P_n + (r-r_n)^2 P_n^{i2} \qquad (55)$$

$$+ 2\frac{(r-r_n)^3}{2} P_n^i P_n^{ii} + \frac{(r-r_n)^4}{4} P_n^{ii2} + \cdots$$

integrating, we then have

$$\int_{r_n-h}^{r_n+h} P^2 dr = Pn^2 2h + \frac{2h^3}{3} P_n^{ii}P_n + \frac{2h^3}{3} P_n^{i2} + \frac{h^5}{10} P_n^{ii2} + \cdots$$

$$= \frac{2h}{3}\left[3Pn^2 + h^2 P_n^{ii}P_n + h^2 P_n^{i2} \right] + \cdots \qquad (56)$$

since

$$h^2 P_n^{ii} = P_{n+1} - 2P_n + P_{n-1}$$

$$= \frac{3h}{3}\left[3Pn^2 + P_n P_{n+1} - 2P_n^2 + P_{n-1}P_n + h^2 P_n^{i2} \right] + \cdots$$

$$= \frac{2h}{3}\left| P_n^2 + P_n P_{n+1} + P_{n-1}P_n + h^2 P_n^{i2} \right| + \cdots$$

$$\sim P_n \frac{h}{3} 2\left[P_n + P_{n+1} + P_{n-1} \right] \quad \text{for } h \ll 1$$

letting

$$\frac{2P_n h}{3} = \frac{h_n^i}{3} \Rightarrow \frac{h_n^i}{3}\left[P_n + P_{n+1} + P_{n-1} \right] \Rightarrow$$

not Simpson's rule.

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However, when point by point is squared and then parabolically integrated, Simpson's rule is applicable and the properties of the recursion formula are preserved.

With this procedure as well as simple arithmetic ones, the following quantities are calculated:

radial electron density $\qquad \Sigma P^2$

number of electrons $\qquad \int_0^x \Sigma P^2 dx$

actual electron density $\qquad -\rho = \Sigma \dfrac{P^2}{4\pi r^2}.$

These quantities contribute to the calculation of the self-consistent potential in the next section.

The previous discussion touched on the determination of polynomial coefficients, but the picture is incomplete since the total power series expressions have not been discussed. Furthermore, initial values for coefficient have not been determined up to this point. Therefore, we will discuss this now.

We can write the quantity g of Equation 58

$$g(r) = - \left[e_i - V - \frac{\ell(\ell+1)}{r^2} \right] = \frac{\ell(\ell+1)}{r^2} - \frac{2z}{r} + \Sigma(m)\, V_m r^m \tag{57}$$

where $V = -\frac{2z}{r}$ has been substituted.

We express P as a power series

$$P = \Sigma(n) p_n r^n \tag{58}$$

We can then express the terms of the series expansion in the radial equation

$$\frac{d^2P}{dr^2} = g(r)P(r) \rightarrow \Sigma(n)(n-1)p_n r^{n-2} = \Sigma(n,m) V_m p_{n-m-2} r^{n-2} \quad (59)$$

where

$$\frac{d^2P}{dr^2} = \Sigma(n)(n-1)p_n r^{n-2} \quad (60)$$

and

$$g(r)P(r) = \Sigma(n,m) V_m p_{n-m-2} r^{n-2} \quad (61)$$

If we define

$$V_{-2} = \ell(\ell+1) \quad (62)$$

$$V_{-1} = -2z \quad (63)$$

$$V_m = 0 \quad \text{for} \quad m < -2 \quad (64)$$

we can then equate the coefficients of equal powers of r in Equations 60 and 61 and obtain the recurrence relations

$$\Sigma(n)n(n-1)p_n r^{n-2} = \sum_n \sum_m V_m \, p_{n-m-2} r^{n-2}$$

or

$$n(n-1) = \sum_m V_m p_{n-m-2} = \Sigma(m) V_m p_{n-m-2} \quad (65)$$

From these recurrence relations, we can find values of all P_n's; once we have started the recurrence, we can get an explicit expression for the power series expansion of the function P.

Writing out Equation 65 explicitly

$$n(n-1)p_n = \ell(\ell+1)p_n - 2z \, p_{n-1} + V_0 p_{n-2} + V_1 p_{n-3} \cdots$$

Combining terms for p_n:

$$[n(n-1) - \ell(\ell+1)] \, p_n = -2z p_{n-1} + V_0 p_{n-2} + V_0 p_{n-3} + \cdots$$

We can expect from our experience with the hydrogenic problem that the first non-vanishing term in the expansion of P will have $n = \ell+1$. For this term, the coefficient $n(n-1) - \ell(\ell+1)$ is zero, so that Equation 67 is identically satisfied with an arbitrary value of $P_{\ell+1}$, combined with $P_n = 0$ for $n < \ell+1$.

The quantity $P_{\ell+1}$ is the arbitrary constant that will eventually be determined to normalize the wave function. We can write the successive equations of Equation 67 in the following form:

$$(0)P_{\ell+1} = 0 \Rightarrow P_{\ell+1} \text{ is arbitrary}$$

$$(2\ell+2)p_{\ell+2} = -2Z p_{\ell+1} \text{ for } n = \ell+1$$

$$2(2\ell+3)p_{\ell+3} = -2z \, p_{\ell+2} + V_0 \, P_{\ell+1}$$

$$3(2\ell+4)p_{\ell+4} = -2z \, p_{\ell+3} + V_0 p_{\ell+2} + V_1 p_{\ell+1}$$

$$4(2\ell+5)p_{\ell+5} = -2z \, p_{\ell+4} + V_0 p_{\ell+3} + V_1 p_{\ell+2} + V_2 p_{\ell+4}$$

Since $P_{\ell+1}$ is arbitrary for $\ell = 0$ (1S electron) we let $p_1 = 1.0000$ and iterate onward.

SECTION V

SYNOPSIS OF SLATER'S APPROACH TO THE CALCULATION OF THE ELECTRONIC STRUCTURE OF ATOMS AND MOLECULES

The highlights of the self-consistent approach are stated here to clarify any problems the reader may incur while pursuing through the general theory. This will help one in not losing sight of the main thrust of the presentation as well as not losing continuity of thought through the labyrinthian paths of the theory as presented previously and in the following sections.

1. THE MANY ELECTRON HAMILTONIAN

The many electron Hamiltonian forms an atomic or molecular system in atomic units:

$$- \sum_i \nabla_i^2 - \sum_{i,a} \frac{zZ_a}{r_{ia}} + \sum_{i \neq j} \frac{2}{r_{ij}} + \sum_{a \neq b} 2\frac{Z_a Z_b}{r_{ab}}$$

(67)

Here the index i refers to the electrons; the index a refers to the nuclei; r_{ia} is the distance between the ith electron and the nucleus a, r_{ij} is the distance between the electrons i and j, and r_{ab} is the distance between nuclei a and b. We also assume that the nuclei are at rest.

When the Hamiltonian is allowed to operate on the product wave function $U_1(1)...U_N(N)$, multiplied by the conjugate of the wave function and integrated over all values of 3N-dimensional space of the 3N electronic coordinates, one has the total energy of the atom or molecule. Additionally, one also has to take into account the antisymmetry of the wave function when the coordinates (and spins) of any two electrons are intercharged - this is the Pauli exclusion principle. It is therefore necessary to write down the many electron wave functions not in the form of a product $U_1(1)...U_N(1)$ but in the form of the Slater determinant

$$\sqrt{\frac{1}{(N!)}} \begin{vmatrix} U_1(1) & U_1(2) & ... & U_1(N) \\ U_2(1) & U_2(2) & ... & U_2(N) \\ \vdots & & & \\ U_N(1) & U_N(2) & ... & U_N(N) \end{vmatrix}$$

(68)

One then can vary the orbitals U_i to minimize the total energy. This total energy has the form

$$\langle E_{HF} \rangle = - \sum_i n_i \int U_i^* \nabla^2 U_i dv - \sum_i n_i \int U_i^* V_N U_i \, dv$$

$$- \frac{1}{2} \sum_i n_i \int U_i^* V_e U_i dv - \frac{1}{2} \sum_{i,j} n_i \, n_j \, \delta(n_{si}, m_{sj})$$

$$\times \int U_i^*(1) \, U_j^*(2) \, \left(\frac{2}{r_{12}}\right) U_j(1)U_i(2) \, dv_1 dv_2 + \sum_{a \neq b} \times \frac{2Z_a Z_b}{r_{ab}} \qquad (69)$$

This Hamiltonian can be explained as follows. Using the fact that the total charge density of all electrons is normally $- \sum_i U_i^* U_i$, where the summation goes over all the occupied orbitals and where the minus sign indicates that the electrons have a negative charge, it has been found more convenient to assign occupation numbers n_i to the states such that unity represents an occupied state and zero an empty one. Then the total electronic charge density is $\rho = - \sum_i n_i U_i^* U_i$ and where the nuclear potential is $V_N = \sum_a \frac{2Z_a}{r_{1a}}$, the electronic potential is $V_e(1) = \int \rho(2) \left(\frac{2}{r_{12}}\right) dv_2$, and $\delta(m_{si} m_{sj})$ indicates that one includes only those pairs of occupied orbitals i,j for which the spin quantum numbers m_{si} or m_{sj} are the same, i.e., pairs of spin orbitals with parallel spins. Furthermore, a correction for the potential acting on the ith electron of position 1 must be taken into account $(V_{xi} = \int U_i^*(2)U_i(2) \left(\frac{2}{r_{12}}\right) dv_2)$. This arises because the electron in one orbital does not act on itself; to see this, let us write

$$V_e(1) + V_{xi}(1) = \int \rho(2) \left(\frac{2}{r_{12}}\right) dv_2 + \int U_i^*(2) \, U_i(2) \left(\frac{2}{r_{12}}\right) dv_2$$

$$= \int \left[- \sum_{j \neq i} n_j \, U_j^*(2) \, U_j(2) \right] \left(\frac{2}{r_{12}}\right) dv_2 \qquad (70)$$

then

$$\int \left[\sum_{j \neq i} n_j \, U_j^*(2) \, U_j(2) \right] dv_2$$

which represents the total charge density at position 2 from (N-1) electrons. The ith electron is being acted upon by the (N-1) other electrons.

The most interesting term in the Hamiltonian is

$$- \frac{1}{2} \sum_{i,j} n_i n_j \; \delta(m_{si}, m_{sj}) \int U_i^*(1) \; U_j^*(2) \; (\frac{2}{r_{12}}) \; U_j(1) \; U_i(2) \; dv_1$$

$$\times \; dv_2 \tag{71}$$

Using the simple case of two electrons whose antisymmetric wave function is $\psi = U_i(1)U_j(2) - U_j(1)U_i(2)$ then the operator average is:

$$\iint \psi^* \; \hat{O} \psi \; dv_1 \; dv_2 = \iint (U_u^*(1) \; U_j^*(2) - U_j^*(1) \; U_i^*(2))$$

$$\times \hat{O} \; (U_i(1) \; U_j(2) - U_j(1) \; U_i(2)) dv_1 \; dv_2$$

$$= \iint \left| U_i^*(1) \; U_j^*(2) \; \hat{O} \; U_i(1) \; U_j(2) + U_j^*(1) \; U_i^*(2) \; \hat{O} \; U_j(1) \; U_i(2) \right.$$

$$- U_i^*(1) \; U_j^*(2) \; \hat{O} \; U_j(1) \; U_i(2) - U_j^*(1) \; U_i^*(2) \; \hat{O} \; U_i(1) \; U_j(2) \tag{72}$$

$$\times \quad dv_1 \; dv_2$$

In the two negative terms we see that an exchange in the positions of the two electrons occurs for the operator $\hat{O}$. In the above case $\hat{O} \equiv \frac{2}{r_{12}}$, a non-differential operator. These exchange terms, as represented by Equation 72 in the general case, can be considered a correction to the direct Coulomb interaction energy due to the Pauli exclusion principle and also contain the simple correction term V_{xi} arising because an electron does not act on itself.

When the Hartree-Fock energy (Equation 69) is minimized with respect to each of the spin orbitals U_i, the resulting one-electron Schrödinger equation is

$$-\nabla^2 U_i - (V_N + V_e) U_i - \sum_j \delta(m_{si}, m_{sj}) \int \left[U_j^*(2) \left(\frac{2}{r_{12}}\right) U_i(2) \, dv_2 \right]$$

$$x \, U_j = \epsilon_i U_i \qquad (73)$$

Equations 69 and 72 constitute the self-consistent Hartree-Fock method. This will be explained in more detail in the next section.

2. THE X-ALPHA METHOD

The x-alpha method is an attempt to simplify the average energy expression by approximating the exchange terms in a certain way. The approximation is based on the theory of the free-electron gas and will be discussed in the next section. However, for comparison with the Hartree-Fock energy (Equation 69) the total energy of the molecule in the $x\alpha$ method is written:

$$<E_{x\alpha}> = -\Sigma(i) n_i \int U_i^* \nabla^2 U_i \, dv$$

$$- \Sigma(i) \, n_i \int U_i^* \Sigma(a) \left(\frac{2Z_a}{r_{1a}}\right) U_i dv + \frac{1}{2} \int \rho(1)\rho(2) \left(\frac{2}{r_{12}}\right) dv_1 \, dv_2$$

$$- \frac{q}{2} \alpha \left(\frac{3}{4\pi}\right)^{1/3} \int \left\{ [- \rho\uparrow(1)]^{4/3} + [-\rho\downarrow(1)]^{4/3} \right\} dv_1$$

$$+ \Sigma(\text{pairs aB, a}\neq B) \frac{2Z_a Z_B}{r_{aB}} \qquad (74)$$

Here n_i and U_i have the same significance as discussed earlier as ρ, Z_a, r_{1a}, r_{12}, and r_{aB}. The quantities $[- \rho\uparrow(1)]^{4/3}$ and $[- \rho\downarrow(1)]^{4/3}$ arise from the product of the quantity $[- \rho\uparrow(1)]^{1/3}$ or $[- \rho\downarrow(1)]^{1/3}$ and the corresponding charge density. The value of the exchange term, the term proportional to α in Equation 74 is based on the theory of the

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free-electron gas. The arrows (↑) and (↓) denote the spin-up and spin-down charge densities, respectively.

From Equations 69 and 74 one can see that the xα method differs from Hartree-Fock only in the exchange term.

3. THE EVALUATION OF THE SELF-CONSISTENT POTENTIAL
   FOR AN ATOM IN THE Xα METHOD

Looking at the various potentials, the calculation of

$$V_N(1) = \frac{2Z}{r_1} \tag{75}$$

is obvious. The evaluation of

$$V_e(1) = \int \rho(r_2)(\frac{2}{r_{12}}) \, dv_2, \text{ is not so obvious.} \tag{76}$$

However, for a spherical distribution $\rho(r_2)$ of charge, we can write

$$V_e(1) = \frac{2}{r_1} \int_0^{r_1} 4\pi r_2^2 \, \rho(r_2) \, dr_2 + \int_{r_1}^{\infty} \frac{2}{r_2} 4\pi r_2^2 \, \rho(r_2) \, dr_2 \tag{77}$$

This expresses the familiar fact that the charge within a sphere of radius r_1, equal to $\int_0^{r_1} 4\pi r_2^2 \rho(r_2) \, dr_2$ exerts a potential at radius r_1 as if it were all concentrated at the center of a sphere, whereas the charge in a spherical shell of radius from r_2 to $r_2 + dr_2$ produces a constant potential at interior points equal to the potential just outside the shell. The integral in the first term of Equation 68 is given as $-\int_0^{r_1} \Sigma P^2 dr$.

The second integral can be immediately computed from Simpson's rule, after constructing a table of functions.

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The second integral can be immediately computed from Simpson's rule, after constructing a table of functions.

The next potential to be considered is

$$V_x = 6\alpha(\frac{3}{8\pi})^{1/3} (- \rho(1))^{1/3}$$

(78)

The charge density $-\rho = \Sigma P^2/4\pi r^2$ can be tabulated so that V_{xi} is essentially computed.

The table can then be set up as

$$r_1 \quad -V_e \quad V_x \quad V_N \quad V_N+V_e \quad V = V_N + V_e + V_x$$

This table will give values of total potential V acting on the electron and its Coulomb part (V_N+V_e).

4. THE TOTAL ENERGY OF AN ATOM

This involves the calculation of various integrals and the methods described in the preceding sections allow us to compute them.

The one-electron Schrödinger equation for the atomic orbital U_i, is

$$\nabla^2 U_i = - (e_i + V)U_i$$

(79)

where

$$V = V_N + V_e + V_x$$

(80)

$$V = \frac{2Z}{r}$$

(81)

$$V_e = \int \rho(r_2)(\frac{2}{r_{12}}) \, dv_2$$

(82)

$$V_x = 6\alpha (\frac{3}{8\pi})^{1/3} \quad [- \rho(1)]^{1/3}$$

(83)

From the previous sections, we have seen how to compute V_e and V_x as functions of r; the computation of V_N is somewhat trivial. If we rewrite the total energy $<E_{x\alpha}>$ in terms of integrals over these potentials, Equation 74 takes the form

$$<E_{x\alpha}< = -\Sigma(i)n_i \int U_i^* \nabla^2 U_i dv - \Sigma(i)n_i \int U_i^* V_N U_i dv$$

$$-\frac{1}{2}\Sigma(i)n_i \int U_i^* V_e U_i dv - \frac{3}{4}\alpha\Sigma(i)n_i \int U_i^* V_x U_i dv \qquad (84)$$

If we multiply Equation 79 by $-U_i^*$ and integrate, we have

$$-\int U_i^* \nabla^2 U_i dv = e_i + \int U_i^* V_n U_i dv + \int U_i^* V_e U_i dv + \int U_i^* V_x U_i dv \qquad (85)$$

Thus, we see that if the U_i's satisfy Equation 67 we can reduce the calculation of $<E_{x\alpha}>$ to the evaluation of the integrals $\int U_i^* V_N U_i dv$, $\int U_i^* V_e U_i dv$ and $\int U_i^* V_x U_i dv$, for the occupied orbitals. For example, the only occupied orbitals for carbon are 1s, 2s and 2p, therefore this means only nine integrals.

Each of the integrands is the product of a charge density $U_i^* U_i$ and a function V_N, V_e or V_x of r only. The integrations over angle, as in the problem of normalization, lead to the result that the integrals in question reduce to $\int_0^\infty P_{1s}^2 V_N dr$, $\int_0^\infty P_{1s}^2 V_e dr$, and so forth. We can multiply at once the functions P_{1s}^2 by V_N or V_e or V_x, and carry out the integrations over r by Simpson's Rule. This procedure is followed in the computer software.

SECTION VI

THE HARTREE-FOCK METHOD AND ITS SIMPLIFICATION

The Hartree equations were obtained by varying the one-electron wave functions $U_1(x)$, $U_2(x)$ ... $U_n(x)$ in such a way as to make the energy $U_1^*(x_1)$ ... $U_n^*(x_n)$ H $U_1(x_1)$ ... $U_n(x_n)$ dx_i ... dx_n an extreme. This was derived earlier.

Similarly, the Hartree-Fock equations, which take into account the antisymmetry properties of the electron wave functions, are obtained by varying the U_is so as to make the energy:

$$\frac{1}{n!} \int \left|\begin{array}{ccc} U_1^*(x_1) & ... & U_1^*(x_n) \\ \hline U_n^*(x_1) & ... & U_n^*(x_n) \end{array}\right| H \left|\begin{array}{ccc} U_1(x_1) & ... & U_1(x_n) \\ \hline U_n(x_1) & ... & U_n(x_n) \end{array}\right| dx_1 \, ... \, dx_n$$

an extremum, where in this latter expression the U's are assumed to be functions depending on coordinates and spins, and where the integrations over the dx's are interpreted to include summing over the spins. The Hartree-Fock equations can then be written in the form:

$$H_1 U_i(x_1) + \left[\sum_{k=1}^{n} \int U_k^*(x_2) \, U_k(x_2) \left(\frac{e^2}{4\pi e_0 r_{12}}\right) dx_2\right] U_i(x_1)$$

$$- \sum_{k=1}^{n} \left[\int U_k^*(x_2) \, U_i(x_2) \left(\frac{e^2}{4\pi e_0 r_{12}}\right) dx_2\right] U_k(x_1) = E_i U_i(x_1) \tag{86}$$

Here H_1 is the kinetic energy operator for the electron of coordinate x_1, plus its potential energy in the field of all nuclei: $\frac{e^2}{4\pi e_0 r_{12}}$ is the Coulomb potential energy of interaction between electrons 1 and 2 expressed in MKS units. The u_i's, as before, are assumed to depend on spin as well as coordinates, and the integrations over dx_2 include summation over spin, so that the exchange terms, the last ones on the LHS of Equation 86 automatically vanish unless the functions U_i and U_k correspond to spins in the same direction.

1. INTERPRETATION OF THE HARTREE-FOCK EQUATIONS

We can subdivide the total density of all electrons into two parts $\rho+$ from those with plus spins, $\rho-$ from those with minus spins; the two together add to the quantity $- e\Sigma(k = 1,...,n)\ U_k^*(x)U_k(x)$. We can show that the Hartree-Fock equation (Equation 86) for a wave function U_i which happens to correspond to an electron with a plus spin is an ordinary Schrödinger equation for an electron moving in a perfectly conventional potential field. This field is calculated by electrostatics from all the nuclei, and from a distribution of electronic charge consisting of the whole of $\rho-$, but of $\rho+$ corrected by removing from the immediate vicinity of the electron, whose wave function we are finding, a correction or exchange charge density whose total amount is just enough to equal a single electronic charge. That is, this corrected charge distribution equals the charge of n-1 electrons as it should. The exchange charge density equals just $\rho+$ at the position of the electron in question, gradually falling off as we go away from that point. We can get a rough idea of the distance in which it has fallen to a small value by replacing it by a constant density $\rho+$ inside a sphere of radius r_0, zero outside the sphere. We have

$$\frac{4}{3} \pi\ r_0^3\ |\rho+|\ = e \text{ or}$$

$$r_0 = \left(\frac{3e}{4\pi|\rho_+|}\right)^{1/3} \tag{87}$$

The situation is then much as if the corrected charge density equaled the actual total electronic charge density outside the sphere, with $\rho-$ within the sphere; this is the Fermi or exchange hole surrounding the electron in question, consisting of a deficiency of charge of the same spin as the electron in question.

This exchange hole is clearly different for wave functions of the two spins, provided $\rho+$ and $\rho-$ are unalike, furthermore, it is different for each dissimilar wave function U_i. It is this difference which leads to the complicated form of the Hartree-Fock equation (this will lead us

to the simplification of using a sort of averaged exchange hole for all the electrons). The exchange holes for dissimilar U_i's of the same spin will only show small differences. We have already seen that the radius r_0 which we obtained by assuming a hole of constant density depends only on $\rho+$ (for a plus spin), and hence, is the same for all U_i's of that spin.

It is this small dependence on U_i which will make it reasonable to simplify the Hartree-Fock equations by using an averaged exchange charge.

To agree with the above description, we expect that the exchange charge density at point x_2, producing a field acting on the electron at x_1, whose wave function $U_i(x_1)$ we are determining by the H-F equation (Equation 86), will have a volume integral equation to $-\rho$ and will be equal when x_2 approaches x_1 to the quantity $-e \sum\limits_{k=1}^{n} U_k^*(x_1) U_k(x_1)$.

To show this we rewrite Equation 86 in the equivalent form

$$
H_1 U_i(x_1) + \left[\sum_{k=1}^{n} \int U_k^*(x_2) U_k(x_2) \left[\frac{e^2}{4\pi\epsilon_0 r_{12}} \right] \right] dx_2 \; U_i(x_1)
$$

$$
- \frac{\left[\sum\limits_{k=1}^{n} \int U_i^*(x_1) U_k^*(x_2) \; U_k(x_1) U_i(x_2) \left[\frac{e^2}{4\pi\epsilon_0 r_{12}} \right] dx_2 \right] U_i(x_1)}{U_i^*(x_1) \; U_i(x_1)}
$$

$$
= E_i U_i(x_1) \tag{88}
$$

The exchange term now appears as a product of a function $U_i^*(x_1)$ times the function $U_i(x_1)$. This exchange potential energy is the potential energy, at the position of the first electron, of the exchange charge density

$$
- e \sum_{k=1}^{n} \frac{U_i^*(x_1) \; U_k^*(x_2) \; U_k(x_1) U_i(x_2)}{U_i^*(x_1) \; U_i(x_1)} \tag{89}
$$

located at the position x_2 of the second electron.

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We note that the exchange charge density depends on the position of the first electron, as well as the second, and also on the quantum state i in which the first electron is located. Furthermore, the total charge is that of a single electron; also, as x_2 approaches x_1, we see at once that the exchange charge density approaches the correct value $-e \sum_{k=1}^{n} U_k^*(x_1)U_k(x_1)$. Thus, we see that the exchange term (Equation 89) satisfies all the conditions necessary to justify our qualitative discussion of its behavior.

2. AVERAGED EXCHANGED CHARGE

The probability that an electron x_1 should be in the i state is evident

$$\frac{U_i^*(x_1)U_i(x_1)}{\sum_j U_j^*(x_1)U_j(x_1)} \tag{90}$$

We can use this quantity as a weighting factor to weigh the exchange charge density (Reference 3). When we do this, we find as the average exchange density, the quantity

$$-e \frac{\sum_{j=1}^{n} \sum_{k=1}^{n} U_j^*(x_1)U_k^*(x_2)U_k(x_1)U_j(x_2)}{\sum_{j=1}^{n} U_j^*(x_1)U_j(x_1)} \tag{91}$$

Using this average exchange charge density, we obtain in place of the Hartree-Fock equations the following Schrödinger equations for the U_i's:

$$H_1 U_i(x_1) + \left\{ \sum_{k=1}^{n} \int U_k^*(x_2)U_k(x_2) \left(\frac{e^2}{4\pi e_0 r_{12}}\right) dx_2 \right.$$

$$\left. - \frac{\sum_{j=1}^{n} \sum_{k=1}^{n} \int U_j^*(x_1)U_k^*(x_2)U_k(x_1)U_j(x_2) \left(\frac{e^2}{4\pi e_0 r_{12}}\right) dx^2}{\sum_{j=1}^{n} U_j^*(x_1)U_j(x_1)} \right\} U_i(x_1) \tag{92}$$

$$= E_i U_i(x_1)$$

The wave functions U_i and energy values E_i, as determined from these equations, will not be quite so accurate as those determined from the H-F equations, but they will at least be much better than those found from the Hartree equations.

One aspect of Equation 92 that will prove to be important is that the functions U_i are all orthogonal to each other.

3. EXCHANGE CHARGE FOR THE FREE-ELECTRON CASE

The calculations of exchange charge and exchange potential which we have been describing can be carried out exactly for the case of the free-electron gas. In turn, the results for the free-electron gas can be directly applied to approximate the exchange potential, with an expression which is much simpler than that appearing in Equation 92.

With this in mind, we now develop the theory of the free-electron gas.

Let us consider a free-electron gas with N electrons in a cube of side L. The Fermi-Dirac distribution function is

$$f^{F-D}(e) = [e^{(e-e_F)kt} + 1]^{-1} g(e) \tag{93}$$

where e_F is a parameter characteristic of the electron gas and $g(\epsilon)$ is the total density of states per unit volume. To calculate the latter we must confine ourselves to the points k which are contained within the surface defined by

$$kx^2 + ky^2 + kz^2 - \frac{2ME}{\hbar^2} = 0 \tag{94}$$

We now wish to determine the number of allowed energy levels in terms of the number of different sets of positive integers (m_x, m_y, m_z) which give rise to independent solutions of the wave equation for free electrons in a box:

$$\nabla^2\psi + \frac{2M}{\hbar^2}(E-V)\psi = 0, \text{ where} \quad \begin{array}{l} V = 0 \ (0 < (x,y,z) < L) \text{ and} \\ V = \infty \text{ elsewhere.} \end{array} \tag{95}$$

Since the solution of Equation 95 is $\psi_{n_x,n_y,n_z}(x,y,z) = (\frac{8}{V})^{1/2}$ x

$\sin k_x x \sin k_y y \sin k_z z$ where $\begin{pmatrix} k_x \\ k_y \\ k_z \end{pmatrix} = \begin{pmatrix} n_x \\ n_y \\ n_z \end{pmatrix} \frac{\pi}{L}$, the energy eigenvalue which

corresponds to the state $(n_x n_y n_z)$ has the form: $E(k) = \frac{\hbar^2 k^2}{2m} = \epsilon =$

$\frac{\hbar^2}{2m} (\frac{\pi}{L}) \frac{(n_x^2 + n_y^2 + n_z^2)}{}$ Since $n_x = \frac{k_x L}{\pi}$, then Equation 94 is

$$n_x^2 + n_y^2 + n_z^2 - \frac{2m}{\hbar^2} \frac{L^2}{\pi^2} \epsilon = 0. \quad (V \text{ is the volume } L^3) \tag{96}$$

Thus, the number of states may be taken to be the volume of the first octant of the sphere in $\vec{n}$ space which is bounded according to the surface (Equation 96).

If we denote the total number of states at the energy ϵ by $\nu(\epsilon)$, then using Equation 96 we have

$$\nu(\epsilon) = \frac{1}{8} \frac{4\pi}{3} n^3 = \frac{\pi}{6} \left(\frac{2m}{\hbar^2} \frac{L^2}{\pi^2} \epsilon\right)^{3/2} = \frac{1}{6\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} V \epsilon^{3/2} \tag{97}$$

$$\rho(\epsilon) = \frac{d\nu(\epsilon)}{d\epsilon} = \frac{1}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} V \epsilon^{1/2} \tag{98}$$

where $n^2 = n_x^2 + n_y^2 + n_z^2$ and $\rho(\epsilon)$ is the density of states of a given spin. Then the total density of states per unit volume is

$$g(\epsilon) = \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \epsilon^{1/2} \tag{99}$$

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and the average value of any physical property $Q(\epsilon)$ associated with the one-electron energy ϵ (per unit volume) is

$$Q = \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty \frac{Q(e)\, e^{1/2} de}{\exp(e-e_F/KT)+1} \qquad (100)$$

The concentration of free electrons according to Equation 93 is:

$$n = \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty \frac{\epsilon^{1/2} de}{\exp\left(\frac{\epsilon-\epsilon_F}{KT}\right) + 1} \qquad (101)$$

and

$$\text{at } T = 0°K, \quad \frac{1}{\exp\left(\frac{e-e_F}{KT}\right) + 1} \qquad (102)$$

therefore, one is for $\epsilon < \epsilon_F$ and zero for $\epsilon > \epsilon_F$ so that the concentration for a highly degenerate electron gas (i.e., one for which $kT \ll \epsilon_F$) is

Thus,

$$n = \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^{e_F} \epsilon^{1/2} de = \frac{1}{3\pi^2} \left(\frac{2m}{\hbar^2}\right) (e_F)^{3/2} \qquad (103)$$

$$e_F = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3} = \frac{\hbar^2 K_F^2}{2m} = \frac{1}{2} m v_F^2 = KT_F$$

or

$$\frac{P_F^2}{2m} = \frac{h^2}{2m} \left(\frac{3\pi^2 n}{1}\right)^{2/3} \frac{1}{4\pi^2} = \frac{h^2}{2m} \left(\frac{3n}{8\pi}\right)^{2/3} \qquad (104)$$

Therefore, the electrons (for the degenerate case) occupy energy values with uniform density in momentum space, out to a level whose energy is $\frac{P_F^2}{2m}$, corresponding to a maximum momentum $P_F = h \left(\frac{3n}{8\pi}\right)^{1/3}$.

The DeBroglie wavelength

$$d = \frac{h}{P_F} = \left(\frac{8\pi}{3n}\right)^{1/3} \qquad (105)$$

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associated with this maximum momentum is related to the radius r_0 of the exchange hole. We notice that for the free-electron gas, the $|\rho+|$ which appeared there equals $\frac{en}{2}$ so that

$$d = \left(\frac{4\pi}{3}\right)^{3/2} r_0 \tag{106}$$

Finally, in order to calculate the exchange term, we can, with negligible loss of accuracy, describe each state by the plane wave

$$\psi_K(r) = \frac{1}{\sqrt{N}} e^{i\vec{K}\cdot\vec{r}} \quad \text{where} \quad \vec{K} = \frac{2\pi}{h} (n_x, n_y, n_z) \text{ and } n_x, n_y \text{ and } n_z \tag{107}$$

are integers. The exchange integral, defined from the exchange term in the H-F Hamiltonian (Equation 88):

$$\epsilon_{ik}^{(x_1)} \equiv - \frac{\int U_i^*(x_1) U_k^*(x_2) \left(\frac{e^2}{4\pi e_0 r_{12}}\right) U_k(x_1) U_i(x_2) dx_2}{U_i^*(x_1) U_i(x_1)}$$

$$e(\vec{K},\vec{K}') = \frac{-\int \psi_k^*(\vec{r}_1) \psi_{k'}^*(\vec{r}_2) \frac{e^2}{4\pi e_0 |r_1 - \vec{r}_2|} \psi_k(\vec{r}_2) \psi_{k'}(\vec{r}_1) dr_2}{\psi_k^*(\vec{r}_1) \psi_k(\vec{r}_1)}$$

$$= \frac{-1}{v^2} \int e^{i(\vec{k}-\vec{k}^\intercal) \circ (\vec{r}_1 - \vec{r}_2)} \frac{e^2}{4\pi e_0 |\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 \tag{108}$$

$$= - \frac{4 e^2}{4\pi e_0 V} \frac{1}{|K-K'|^2}$$

The minus sign indicates a decrease in the electron-electron interaction between electrons of the same spin because of the Pauli principle.

If $\vec{K}$ is the wave vector for a given electron, then $\vec{K}$ is an index denoting wave vectors for all other electrons in the system. From Equation 88, the total exchange interaction acting on a single electron is then obtained by summing over states $\vec{K}$'s. The summation can be replaced by an integration, since

$$\sum_{\vec{K}} \rightarrow \frac{V}{(2\pi h)^3} \int d\vec{p} = \frac{V}{(2\pi)^3} \int d\vec{K} \tag{109}$$

Using Equations 109 to 108, the total exchange energy acting on a single electron is thus

$$\sum_{\vec{K}'} \epsilon(K, \vec{K}') = \frac{-e^2}{4\pi e_0 (2\pi)^2} \int_0^{K_F} \frac{d\vec{K}'}{|\vec{K} - \vec{K}'|^2}$$

$$= \frac{-e^2}{(4\pi e_0 (2\pi)^2} \int_0^{2\pi} d\ell \int_0^{\pi} \sin\theta d\theta \int_0^{K_F} \frac{K'^2 dK'}{K^2 + K'^2 - 2KK'\cos\theta} = \epsilon(\vec{K}) \tag{110}$$

where K_F is the Fermi wave vector, i.e.,

$$K_F \rightleftharpoons \sqrt{\frac{2me_F}{\hbar^2}} \tag{111}$$

Evaluation of the integral is straightforward but lengthy and

$$\text{gives} \quad \epsilon(\vec{K}) = \frac{e^2 K_F}{(2\pi)4\pi e_0} \left(2 + \frac{K^2 - K_F^2}{K K_F} \ln \frac{|K_F - K|}{K_F + K} \right) \tag{112}$$

The exchange potential energy can be conveniently stated in terms of the ratio $\eta = \frac{p}{p_F}$ of the magnitude of the momentum of the electron to the maximum momentum corresponding to the top of the Fermi distribution.

The exchange potential energy $= -\left(\dfrac{e^2}{4\pi\epsilon_0}\right)\left(\dfrac{4P_F}{h}\right) F(\eta)$ \hfill (113)

$$= -\left(\frac{6}{\pi}\right)^{2/3} \left(\frac{e^2}{4\pi\epsilon_0 r_0}\right) F(\eta)$$

where

$$F(\eta) = \frac{1}{2} + \frac{1-\eta^2}{4\eta} \ln\left[\frac{1+\eta}{|1-\eta|}\right] \hspace{2cm} (114)$$

The function $F(\eta)$ is shown in Figure 1. It goes from unity when $\eta = 0$ for an electron of zero energy to $\frac{1}{2}$ when $\eta = 1$, at the top of the Fermi distribution.

We see that this exchange potential energy is of the form which we expect. If we had a sphere of radius r_0, filled with uniform charge density $|\rho+| = \frac{ne}{2}$, the potential energy of an electronic charge at the center of the sphere would be $-\frac{3}{2}\left(\frac{e^2}{4\pi\epsilon_0 r_0}\right)$, while the value of Equation 113 is $-1.54\left(\frac{e^2}{4\pi\epsilon_0 r_0}\right)$ at the bottom of the Fermi band and half this value at the top. Thus, this simple model of an exchange hole of constant charge density gives not only a qualitatively correct value for the exchange potential but also a rather accurate quantitative value; and the extreme difference between top and bottom of this band corresponds only to a factor of 2 in the exchange potential. If we average overall wave functions, we find that the properly weighted average of $F(\eta)$ is 3/4.

Thus the exchange potential energy of the averaged exchange charge is

$$e_{av} = -\left(\frac{3}{4}\right)\left(\frac{6}{\pi}\right)^{2/3}\left(\frac{e^2}{4\pi\epsilon_0 r_0}\right)$$
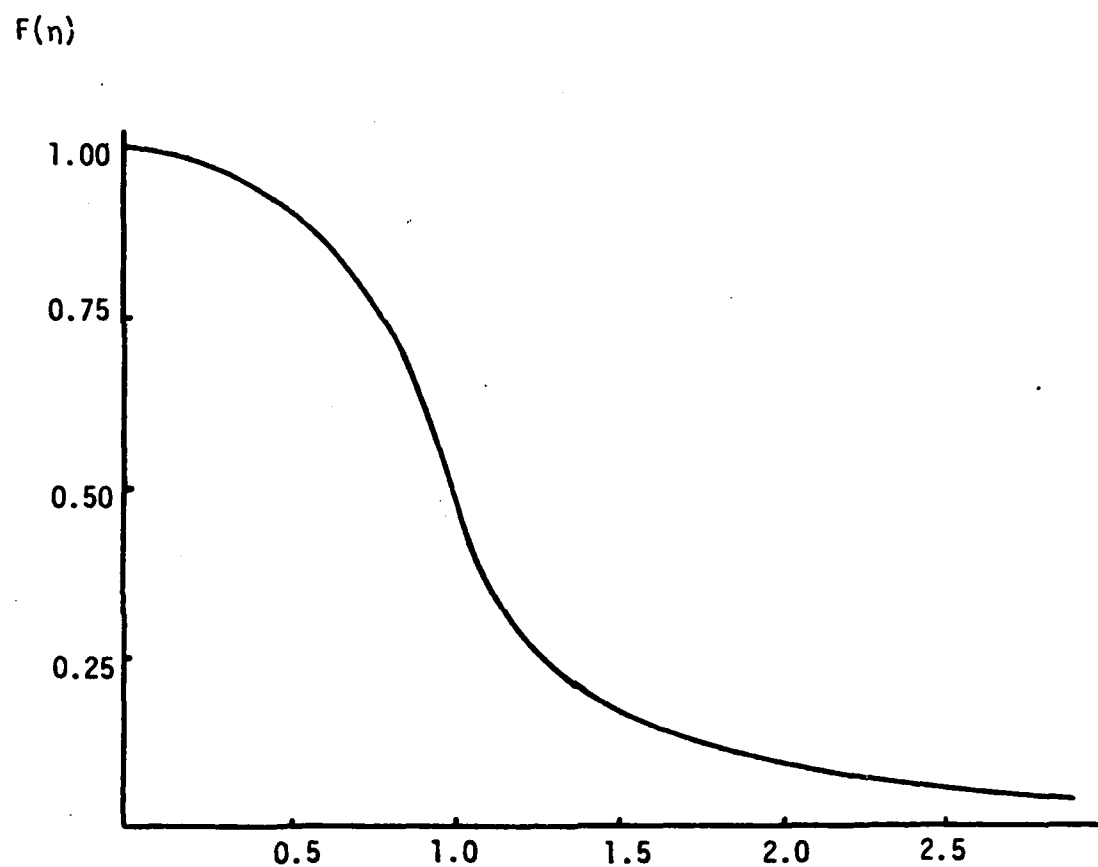
\hfill (115)

Figure 1. Graph of the Exchange Energy Coefficient F(η)

4. THE USE OF THE FREE-ELECTRON APPROXIMATION FOR THE EXCHANGE POTENTIAL

It is clear that the exchange charge density (Equation 91) and the corresponding potential appearing in Equation 92 must depend on the density of electronic charge, but not greatly on anything else. Thus, in no case will we expect it to be very different than what we should have in a free-electron gas of the same charge density. For a non-spin polarized system, in which $\rho+ = \rho^- = \frac{\rho}{2}$, we may approximate the averaged exchange potential by what we should have in a free-electron gas of the same density. Thus, combining Equations 87 and 115, we have

$$e_{av}(x) = -\frac{3}{4} \left(\frac{6}{\pi}\right)^{3/2} \left[\frac{e^2}{4\pi e_0 r_0}\right] = -3 \left[\frac{e^2}{4\pi e_0}\right] \left[\frac{3\rho(x)}{8\pi}\right]^{1/3} \tag{116}$$

where $\rho(x)$ is the local electron number density at point x. If we recall that this is $\sum_k U_k^*(x)U_k(x)$ we finally have our simplified Schrödinger equation for the one-electron function U_i, to replace Equation 92

$$H_1 U_i(x) + \sum_K \int U_k^*(x_2)U_k(x_2) \left[\frac{e^2}{4\pi e_0 r_{12}}\right] dx_2 \tag{117}$$

$$-3 \left(\frac{e^2}{4\pi e_0}\right) \left[\frac{3}{8\pi} \sum_k U_k^*(x_1)U_k(x_1)\right]^{1/3} U_i(x_1) = E_i U_i(x_1)$$

This equation is in practice a simple one to apply. We solve it for each of the wave functions U_i, then find the total charge density arising from all these wave functions and then calculate the potential energy, including the exchange term, to go into Equation 117, so as to check the self-consistency of the solution. We can change to atomic units by setting $\frac{e^2}{4\pi e_0}$ to 2.

This method will facilitate an explicit self-consistent formulation for the case of atoms as follows. Let the electrostatic potential of the nucleus, and of all electrons, at distance r from the nucleus of the

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spherical atom, be $\dfrac{Z_p(r)e}{4\pi\epsilon_0 r}$. Then the charge density is given by Poisson's equation as

$$\rho = - \, e_0 \nabla^2 \, (\frac{z_p e}{4\pi e_0 r}) \tag{118}$$

When we express the Laplacian in spherical coordinates, this gives

$$\rho = - \, (\frac{e}{4\pi}) \, (\frac{1}{r}) \, \frac{d^2 z_p}{dr^2} \tag{119}$$

The exchange potential energy becomes

$$\epsilon_{av} = -3 \, (\frac{e^2}{4\pi\epsilon_0}) \, [\frac{3\rho}{8\pi}]^{1/3} = -3 \, (\frac{e^2}{4 \, e_0}) \, \left[\frac{3}{8\pi} \cdot \frac{1}{4\pi} \cdot \frac{1}{r} \frac{d^2 z_p(r)}{dr^2}\right]^{1/3}$$

$$= -3 \, (\frac{e^2}{4\pi\epsilon_0}) \, \left|\frac{3}{32\pi^2} \cdot \frac{1}{r} \frac{d^2 z_p(r)}{dr^2}\right|^{1/3} \tag{120}$$

and finally, the total potential energy, for use in the Schrödinger equation for $U_i(x_i)$ is

$$- \frac{e^2}{4\pi\epsilon_0 r} \left[z_p + 3 \, (\frac{3}{32\pi^2})^{1/3} \, \left(r^2 \frac{d^2 z_p}{dr^2}\right)^{1/3}\right] \tag{121}$$

To carry out a self-consistent solution for an atom using this method, we find $Z_p(r)$ such that the wave functions U_i, determined from a single Schrödinger equation using the potential energy (Equation 121) added to give a charge density which would lead by Poisson's equation back to a potential energy $(\dfrac{-e^2 Z_p}{4\pi\epsilon_0})$.

When this procedure is carried out for the atoms of the various elements, it is found that the ground-state energy of an atom is consistently greater than that obtained in the Hartree-Fock approximation. Since the H-F equations satisfy a variational principle, they must give an upper bound to the energy of the ground state. To improve the

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agreement with $\langle E_{HF} \rangle$, the above approximate treatment of exchange is modified by including a parameter α to represent the effects of the non-free electron nature of the system. The value of α is determined by setting the atomic ground-state energy equal to the Hartree-Fock value. This results in α values ranging from about 0.75 for the lighter elements to about 0.69 for the heavier elements.*

If one also takes into account spin polarization of the electrons, then the final form of Slater's x_α local approximation to the exchange potential at point x for an electron of spin up or down is, in atomic units,

$$V_{x\alpha}(x) = -6\alpha \left(\frac{3\rho(x)}{4\pi}\right)^{1/3}$$

(122)

where $\rho(x)$ denotes the appropriate spin-up or spin-down electron number density at x.

Equation 92 for the one-electron orbitals U_i and energies E_i of an atom or molecule becomes

$$[H_1 + V_e(x_1) + V_{x\alpha}(x_1)] U_i(x_1) = E_i(x_1)$$

(123)

with V_e given by Equation 96 and $V_{x\alpha}$ by Equation 122, and with total energy $\langle E_{x\alpha} \rangle$ as given in Equation 94.

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*The α coefficient can also be chosen so as to satisfy the virial theorem, $\langle T \rangle = -\ 1/2\ \langle V \rangle$, where, $\langle T \rangle$ and $\langle V \rangle$ are respectively the average kinetic and potential energies. This theorem must hold for the true ground state of any system, such as an atom, in which the interactions are all Coulombic. The values of α determined in this way are essentially the same as those determined by the first method.

SECTION VII

SIMPLE SCATTERING THEORY

We shall consider the scattering of a stream of charge particles by a small spherically symmetrical region in which the potential energy is different from zero.

In experiments on the scattering of a beam of particles, one measures the number of scattered particles falling per unit time on an area ds placed at a distance r from the scattering atoms. The number of particles falling on ds is proportional to the area ds and inversely to the square of the distance r. We shall refer to the particles which hit ds as "scattered through an angle θ into the solid angle $d\omega$." This number of particles scattered into $d\omega$ is also proportional to the current per unit area in the incident beam. Suppose that N particles cross unit area per unit time in the incident beam. Let the number of particles scattered per unit time through an angle θ into the solid angle $d\omega$ be:

$$NI(\theta)d\omega \qquad (124)$$

Then $I(\theta)$ is the quantity we wish to calculate. $I(\theta)\, d\omega$ has the dimensions of area and is called the effective cross-section for scattering into the solid angle $d\omega$ or as the differential cross-section.

Let (x,y,z) denote Cartesian coordinates of the electron and (r,θ,ϕ) its spherical polar coordinates. We shall suppose the atom to be situated at the origin, and the potential energy of an electron distance r from the origin to be $V(r)$. We shall also assume that $V(r)$ tends to zero faster than $1/r$; the case of Coulomb scattering will be addressed later. We represent the stream of electrons by the plane wave $\exp(iKz)$ where K is equal to $\frac{2\pi mv}{h} = \frac{2\pi P}{h}$. This wave represents a density of electrons per unit volume, and therefore a flow of v electrons across unit area per unit time. The wave will be scattered by the atom, the amplitude of the scattered wave at the point (r, θ, ϕ) being

$$\frac{f(\theta)e^{iKr}}{r} \qquad (125)$$

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that is, the plane wave will be scattered as a "wavelet" by Huygen's principles or $\dfrac{e^{iKr}}{r}$ but whose direction is modified through a given angle θ. Our problem is to find $f(\theta)$. From it we can deduce the number scattered into a given solid angle per unit time. The number of electrons in the scattered wave crossing an element of area ds at the point (r, θ, ϕ) is $\dfrac{v}{2}$ ds $|f(\theta)|^2$ per unit time; and therefore, if the incident beam is such that <u>one</u> electron falls on unit area per unit time, the number $I(\theta)d\omega$ scattered into a given solid angle $d\omega$ per unit time is equal to $|f(\theta)|^2 d\omega$. Therefore, $I(\theta) = |f(\theta)|^2$. The number of particles scattered between angles θ and $d\theta + \theta$ is $|f(\theta)|^2 2\pi\sin\theta d\theta$. Our problem is to find a solution Ψ of the wave equation which, at a large distance from the atom, represents an incident wave and a scattered wave, or for large r,

$$\Psi \sim e^{iKz} + \frac{e^{iKr}f(\theta)}{r} \qquad (126)$$

The wave equation satisfied by Ψ may be written as

$$\nabla^2\Psi + [K^2 - U(r)]\Psi = 0$$

where

$$K = \frac{mv}{\hbar}; \quad U(r) = \frac{2m}{\hbar^2} V(r) \qquad (127)$$

Before considering the solution of Equation 127, we require a certain expansion in spherical harmonics of e^{iKz} which will now be proved and which permeates many discussions to follow.

The plane wave e^{iKz} is a solution of the equation

$$\nabla_z^2\Psi + K^2\Psi = 0 \qquad (128)$$

with axial symmetry. This equation can also be solved in spherical coordinates; its solution is

$$\Psi = P_\ell(\cos\theta)f_\ell(r) \qquad (129)$$

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if f_ℓ is a solution of the equation, then

$$\frac{1}{r^2} \frac{d}{dr} (r^2 \frac{df}{dr}) + (K^2 - \frac{\ell(\ell+1)}{r})f = 0 \qquad (130)$$

where $P_\ell(\cos\theta)$ is the ℓth Legendre coefficient. That is,
$f_0 = e^{iKz}$ for $\nabla_r^2 \psi + (K^2 - \frac{\ell(\ell+1)}{r^2})$ f_ℓ for $\ell = 0$, a less general case.

Equation 130 can be solved in series; there are two solutions, one
beginning with r^ℓ and the other with $r^{-\ell-1}$. Let us denote by $f_\ell(r)$ the
solution Equation 130 that is <u>bounded</u> at $r = 0$. Then, except for an
arbitrary constant, $f_\ell(r)$ is determined.

If A_ℓ are arbitrary constants, $\sum\limits_{\ell=0}^{\infty} A_\ell P_\ell(\cos\theta)f_\ell(r)$ is a solution
of Equation 128 and we know that this is the most general solution of
Equation 128 which has axial symmetry (i.e., does not involve ϕ) and
which is finite at the origin. [Note: The key is that $\nabla_z^2 \to \nabla_r^2$ (spherical
Laplacian), a more general case, with the restriction that f_ℓ is bounded
at the origin. (Being bounded at the origin implies that $f_\ell(r)$ has a
power series expansion such that the pole $\frac{\ell(\ell+1)}{r^2}$ is eliminated.]

It follows that e^{iKz} can be expanded in the form:

$$e^{iKz} = e^{iKr\cos\theta} = \sum\limits_{\ell=0}^{\infty} A_\ell P_\ell(\cos\theta)f_\ell(r) \qquad (131)$$

To obtain A_ℓ, we multiply both sides by $P_\ell(\cos\theta)\sin\theta$ and integrate
0 to π. Putting $\cos\theta = t$, we obtain

$$\int_{-1}^{1} e^{iKrt'}P_\ell(t')dt' = \int_{-1}^{1} \sum\limits_{\ell=0}^{\infty} f_\ell A_\ell P_\ell(t)P_\ell(t')dt' \qquad (132)$$

Since $\int_{-1}^{1} P_\ell(t)P_\ell(t')dt' = \frac{2\delta tt'}{2\ell+1}$ by orthogonality of Legendre
functions, we have

$$\int_{-1}^{1} e^{iKrt}P_\ell(t)dt = \frac{2}{2\ell+1} A_\ell f_\ell(r) \qquad (133)$$

We can define $f_\ell(r)$ exactly by means of its asymptotic expansion for large r; integrating the left-hand side of Equation 133, we have

$$\int_{-1}^{1} e^{iKrt} P_\ell(t)dt = \frac{e^{iKrt}}{iKr} P_\ell(t) \Big|_{-1}^{1} - \frac{1}{iKr} \int_{-1}^{1} e^{iKrt} \frac{d\, P_\ell(t)}{dt} \, dt$$

$$= \frac{e^{iKr} P_\ell(1) - e^{-iKr} P_\ell(-1)}{iKr} - \frac{1}{iKr} \int_{-1}^{1} e^{iKr} P_\ell'(t)dt$$

(134)

Noting that $P_\ell(1) = 1$; $P_\ell(-1) = (-1)$ and the asymptotic property

$$\lim_{r \to \infty} \frac{1}{iKr} \int_{-1}^{1} e^{iKr} P_\ell'(t)dt = \lim_{r \to \infty} \frac{1}{iKr} \left\{ \frac{e^{iKz}}{iKr} P_\ell'(t) - \frac{1}{iKr} \right.$$

(135)

$$\left. \int_{-1}^{1} e^{iKr} P_\ell''(t)dt \right\} \to 0$$

then Equation 134 equals

$$\frac{e^{iKr} - (-1)^\ell e^{iKr}}{iK} \quad \text{since } (-1)^\ell = e^{+\pi i \ell}$$

we have

$$\frac{e^{iKr} - (-1)^\ell e^{-iKr}}{iKr} = \frac{e^{iKr} - e^{+\pi i \ell} e^{-iKr}}{iKr}$$

$$= \frac{e^{-\frac{\pi i \ell}{2}} e^{iKr} - e^{+\frac{\pi i \ell}{2}} e^{-iKr}}{e^{-\frac{\pi i \ell}{2}} iKr} = \frac{2e^{\frac{\pi i \ell}{2}} \sin(Kr - \frac{\pi \ell}{2})}{Kr}$$

(136)

$$= \frac{2(i)^\ell \sin(Kr - \frac{\pi \ell}{2})}{Kr}$$

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therefore

$$\frac{2}{2\ell+1} A_\ell f_\ell(r) = \int_{-1}^{1} e^{iKrt} P_\ell(t)dt = \frac{2(i)^\ell \sin(Kr - \frac{\pi\ell}{2})}{Kr}$$

or

$$f_\ell(r) = \frac{\sin(Kr - \frac{\pi\ell}{2})}{Kr} \quad \text{and} \quad \frac{2A_\ell}{2\ell+1} = 2(i)^\ell \quad \text{or} \quad A_\ell = (2\ell+1)(i)^\ell$$

therefore

$$e^{iKz} = \sum_{\ell=0}^{\infty} (2\ell+1)(i)^\ell P_\ell(\cos\theta) f_\ell(r) \tag{137}$$

for

$$\ell = 0 \quad f_0 = \frac{\sin Kr}{Kr} = j_0(Kr) \tag{138}$$

and

$$f_\ell(r) = (\frac{\pi}{2Kr})^{1/2} J_{\ell+1/2}(Kr) = j_\ell(Kz) \tag{139}$$

We can look at the general solution of Equation 127

$$\nabla^2 \psi + [K^2 - U(r)]\psi = 0$$

[NOTE: $\nabla^2 \equiv \nabla_r^2$ and is not necessarily a spherical operator here]. $\tag{127}$

As before, the general solution of Equation 127 having axial symmetry is

$$\psi = \sum_{\ell=0}^{\infty} A_\ell P_\ell(\cos\theta) L_\ell(r) \tag{140}$$

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where A_ℓ are arbitrary constants, and L_ℓ is any solution of

$$(\frac{1}{r^2} \frac{d}{dr} \ (r^2 \frac{dL_\ell}{dr}) + (K^2 - U(r) - \frac{\ell(\ell+1)}{r^2}) \ L_\ell = 0 \qquad (141)$$

As before, Equation 141 has two independent solutions, one finite at the origin and the other infinite.

We wish to choose the constants A_ℓ so that Equation 140 shall represent an incident wave and a scattered wave, i.e., so that Equation 140 shall have the asymptotic form of $\psi \sim e^{iKz} + \frac{e^{iKr}}{r} f(\theta)$. It is necessary that our wave function should be finite everywhere, L_ℓ must therefore be chosen to be a solution of Equation 141 that is finite at the origin. If se set $L_\ell(r) = \frac{G_\ell(r)}{r}$,

$$\frac{dL_\ell}{dr} = \frac{1}{r} \frac{dG_\ell}{dr} - \frac{G_\ell}{r^2}$$

$$\frac{d^2L_\ell}{dr^2} = -\frac{1}{r^2} \frac{dG_\ell}{dr} + \frac{1}{r} \frac{d^2G_\ell}{dr^2} - \frac{dG_\ell}{r^2 dr^2} + \frac{2G_\ell}{r^3}$$

$$= -\frac{2dG_\ell}{r^2 dr} + \frac{1}{r} \frac{d^2G_\ell}{dr^2} + \frac{2G_\ell}{r^3}$$

Substituting into Equation 141 we have

$$\frac{1}{r^2} (2r \frac{dL_\ell}{dr} + r^2 \frac{d^2L_\ell}{dr^2}) + (K^2 - U(r) - \frac{\ell(\ell+1)}{r^2})L_\ell = 0$$

$$=> \frac{1}{r^2} \left[2r \cdot \frac{1}{r} \frac{dG_\ell}{dr} - \frac{2rG_\ell}{r^2} + r^2 (\frac{-2}{r^2} \frac{dG_\ell}{dr} + \frac{1}{r} \frac{d^2G_\ell}{dr^2} + \frac{2G_\ell}{r^3}) \right]$$

$$+ \frac{K'^2 G_\ell}{r} = 0$$

$$= \frac{1}{r} \frac{d^2G_\ell}{dr^2} + (K^2 - U(r) - \frac{\ell(\ell+1)}{r^2}) \frac{G_\ell}{r} = 0$$

or

$$\frac{d^2 G_\ell}{dr^2} + \left(K^2 - U(r) - \frac{\ell(\ell+1)}{r^2}\right) G_\ell = 0 \qquad (142)$$

For large r, the last two terms in the parenthesis tend to be zero, thus we should expect that the asymptotic form of any solution G would be a solution of $\frac{d^2 G_\ell}{dr^2} + K^2 G_\ell = 0$ or $G_\ell = A_1 \cos Kr + B_1 \sin Kr \to A \sin(Kr + \epsilon)$ where A and ϵ are constants.

To test whether this is so, we set

$$G = U(r)e^{iKr} \qquad (143)$$

substituting into Equation 142 we have

$$\frac{dG}{dr} = U'e^{iKr} + Uike^{iKr}$$

$$\frac{d^2 G}{dr^2} = U''e^{iKr} + 2iKU'e^{iKr} - K^2 U e^{iKr}$$

or

$$U'' + 2iKU' - K_U^2 + K^2 U - Uu - \frac{\ell(\ell+1)}{r^2} U = 0 \qquad (144)$$

or

$$U'' + 2iKU' - Uu - \frac{\ell(\ell+1)U}{r^2} = 0$$

$$U'' + \frac{2IKdu}{dr} - \left[u + \frac{\ell(\ell+1)}{r^2}\right] U = 0 \qquad (145)$$

For large r, we may assume, since u is nearly constant, that

$$\frac{d^2 U}{dr^2} \ll \frac{KdU}{dr}.$$

Neglecting the former term, we can integrate Equation 145

$$2rK \frac{dU}{dr} = [u + \frac{\ell(\ell+1)}{r^2}] U = 0$$

$$2rk \frac{dU}{u} = [u + \frac{\ell(\ell+1)}{r^2}] dr$$

Integration gives

$$2iK \log U = \int^r [u(r) + \frac{\ell(\ell+1)}{r^2}] dr \tag{146}$$

$$\therefore U = \exp \frac{-i}{2K} \int^r [u(r) + \frac{\ell(\ell+1)}{r^2}] dr \tag{147}$$

The right-hand side of Equation 145 tends to a constant for large r if and only if $u(r)$ tends to zero faster than $\frac{1}{r}$ as r tends to infinity. Thus, for fields which fall to zero faster than the Couloumb field, G, the asymptotic form is: $G = A \sin(Kr+e)$.

The particular solution of Equation 142 that is finite at the origin will then have the form $\dfrac{C\sin(Kr - 1/2\ \ell\pi + N_\ell}{K}$ where C is an arbitrary constant and N is a constant that depends on K and $u(r)$. [NOTE: the term $-\frac{1}{2} \ell\pi$ is added so that, if $u(r)$ is zero, N_ℓ shall be zero. The reader may feel that this is handwaving, however, this form shall be proven in Appendix A through perturbation theory].

We have to choose the constants A in Equation 139. If we subtract the expansion for e^{iKz} for the incident wave, we obtain the expression for the scattered wave. We shall use the following equations,

$$\psi = \sum_{\ell=0}^{\infty} A_\ell L_\ell(r)P_\ell(\cos\theta) \tag{148}$$

$$L_\ell(r) = \frac{\sin(Kr - 1/2\ \ell\pi + N_\ell)}{Kr} \tag{149}$$

$$e^{iKz} = \sum_{\ell=0}^{\infty} (2\ell+1) \ i^{\ell} P_{\ell}(\cos\theta) f_{\ell} \tag{150}$$

$$\psi \sim e^{iKz} + \frac{f(\theta)e^{iKr}}{r} \tag{151}$$

together with the fact that there must be no terms proportional to $\frac{e^{-iKr}}{r}$ in the asymptotic expansion of the scattered waves since these can be shown to correspond to incident waves. Therefore, looking at the ℓth component:

$$A_{\ell}L_{\ell}(r) \sim e^{iKz} + C_{\ell} \frac{e^{iKr}P_{\ell}(\cos\theta)}{r} = e^{iKz} + \frac{f(\theta)e^{iK\cdot r}}{r} \tag{152}$$

then

$$A_{\ell}L_{\ell}(r) - e^{iKz} = C_{\ell} \frac{e^{iKr}P_{\ell}(\cos\theta)}{r} \tag{153}$$

or

$$\left\{ A_{\ell} \frac{e^{iKr - 1/2\ell\pi i + N_{\ell}i}}{2iKr} - A_{\ell} \frac{e^{-iKr + i/2\ell\pi - iN_{\ell}}}{2iKr} - (2\ell+1)i^{\ell}f_{\ell} \right\}$$

$$\times P_{\ell}(\cos\theta) = C_{\ell} \frac{e^{iKr}}{r} P_{\ell}(\cos\theta) \tag{154}$$

since $f_{\ell} = \frac{\sin}{Kr}(Kr - \frac{\ell\pi}{2}) = \dfrac{e^{iKr - \frac{\pi\ell i}{2}} - e^{-iKr + \frac{\pi\ell}{2}}}{2iKr}$

substituting this into Equation 154 we have

$$\left\{ A_{\ell} \frac{e^{iKr - \frac{\pi\ell i}{2} + N_{\ell}i}}{2iKr} - (2\ell+1)\ i^{\ell} \frac{e^{iKr - \frac{\pi\ell i}{2}}}{2iKr} \right\} P_{\ell}(\cos\theta)$$

$$- \left\{ A_{\ell} \frac{e^{-iKr + \frac{i\ell\pi}{2} - iN_{\ell}}}{2iKr} - (2\ell+1)i^{\ell} \frac{e^{-iKr + \frac{\pi\ell i}{2}}}{2iKr} \right\} P_{\ell}(\cos\theta) \tag{155}$$

$$= C_{\ell} \frac{e^{iKr}}{r} P_{\ell}(\cos\theta)$$

Matching terms of $\dfrac{e^{iKr - n\ell i}}{2}$ and $\dfrac{e^{-iKr + i}}{2}$ we have

$$\frac{1}{2iK}\left\{ A_\ell\, e^{iN_\ell} - (2\ell+1)i^\ell \right\}\frac{e^{iKr - \frac{\pi\ell i}{2}}}{1} = C_\ell\, e^{iKr} \tag{156}$$

$$\frac{1}{2iK}\left\{ A_\ell\, e^{-N_\ell i} - (2\ell+1)i^\ell \right\} = 0 \quad \text{from Equation 157} \tag{157}$$

$$A_\ell = (2\ell+1)i^\ell\, e^{iN_\ell}$$

Substituting Equation 157 into Equation 156 we have

$$i^\ell\,\left(\frac{2\ell+1}{2iK}\right)(e^{2iN_\ell} - 1)\, e^{-\frac{\pi\ell i}{2}} = C_\ell \tag{158}$$

In Equation 158 the terms i^ℓ and $e^{-\frac{\pi\ell i}{2}}$ can be combined as

$$(e^{\frac{\pi\ell i}{2}})(e^{-\frac{\pi\ell i}{2}}) = 1 \quad \therefore$$

$$\left(\frac{2\ell+1}{2iK}\right)(e^{2iN_\ell} - 1) = C_\ell \tag{159}$$

Therefore the final equation from Equations 148 and 151 is:

$$\psi = \sum_{\ell=0}^{\infty} (2\ell+1)i^\ell L_\ell(r)P_\ell(\cos\theta) \quad \text{since} \quad \frac{f(\theta)e^{iKr}}{r} = \frac{C_\ell e^{iKr}}{r}$$

we have at last

$$f(\theta) = \frac{1}{2iK}\sum_{\ell=0}^{\infty} (2\ell+1)(e^{2iN_\ell} - 1)P_\ell(\cos\theta) \tag{160}$$

This last expression gives us the expression for the amplitude of
the scattered wave. It should be noted that $f(\theta)$ is complex; the
scattered intensity $I(\theta)$ is given by the square of the modulus or:

$$f_\ell(\theta)f_\ell^*(\theta) = \frac{1}{4K^2}(2\ell+1)^2(e^{2iN_\ell}-1)(e^{-2iN_\ell}-1)P_\ell^2(\cos\theta)$$

since

$$(e^{2iN_\ell}-1)(e^{-2iN_\ell}-1) = 1 - (e^{2iN_\ell}+e^{-2iN_\ell}) + 1 = 2 - 2\cos2N_\ell$$

then

$$|f_\ell(\theta)|^2 = \frac{1}{2K^2}(2\ell+1)^2(1-\cos2N_\ell)$$

integrating over all solid angles

$$Q = \sum_{\ell=0}^{\infty} 2\pi \int_0^\pi |f_\ell(\theta)|^2 \sin\theta d\theta = \sum_{\ell=0}^{\infty} 2\pi \int_0^\pi \frac{(2\ell+1)^2 \cdot 2}{2K^2} \sin^2N_\ell P_\ell^2(\cos\theta)\sin\theta d\theta$$

$$= \frac{2\pi}{K^2} \sum_{\ell=0}^{\infty} (2\ell+1)^2 \sin^2N_\ell \int_0^\pi P_\ell^2(\cos\theta)\sin\theta d\theta$$

since the integral

$$\int_0^\pi P_\ell^2(\cos\theta)\sin\theta d\theta = \frac{2\ell}{2\ell+1} \text{ we have } Q = \frac{4\pi}{K^2} \sum_{\ell=0}^{\infty} (2\ell+1)\sin^2N_\ell$$

[NOTE: The author feels that for a complete exposition of scattering
theory it was necessary to derive the steps leading to the scattering
amplitude Q. This section will eventually lead into the Generalized
Theory of Scattering which is the crux of the theoretical foundation
laid for the understanding of the computational approach to the solution
of the carbon complex. However, $|f(\theta)|^2$ or the scattered amplitude is
not addressed in the computer programs nor is it used explicitly in any
of the calculations. If $|f(\theta)|^2$ were used, it would define the in situ
location of charge densities in the carbon complex; however, for multi-
center computations, $|f(\theta)|^2$ would be untenably complicated.]

1. THE BORN SERIES AND T-MATRIX

The standard problem of the one-particle in quantum theory is the effect produced upon a free particle by a local potential $V(\underline{r})$.

It has been taught that we should tackle the problem by looking at solutions of the corresponding Schrödinger's equation with various boundary conditions. However, the Green's function method if often more powerful. Since it has already been discussed, we shall continue in this respect.

Looking at the Schrödinger equation

$$H\psi = \epsilon\psi \quad \text{and} \quad (1') \quad H_0\psi_m(\underline{r}) = \epsilon_m\psi_m(\underline{r}) \tag{161}$$

then subtracting, we have

$$(\epsilon - H)\psi = 0 \tag{162}$$

Considered as an operator, the Green's function satisfies

$$(\epsilon - H)G = 1 \tag{163}$$

$$\Rightarrow G(\epsilon) = \frac{1}{H - \epsilon} = \frac{1}{\epsilon - H_0 - V} \tag{164}$$

if V were in some sense "small", this could be expanded in an infinite series

$$G(\epsilon) = \left\{ \frac{1}{\epsilon - H_0} \quad \frac{1}{1 - \frac{V}{\epsilon - H_0}} \right. = \left\{ \frac{1}{\epsilon - H_0} \right\} \times$$

$$\left\{ 1 + 1 \, \underline{V} \, \frac{1}{\epsilon_0 - H_0} + 1 \, V \, \frac{1}{\epsilon_0 - H_0} \, V \, \frac{1}{\epsilon - H_0} \right\} \tag{165}$$

$$= \frac{1}{\epsilon - H_0} + \frac{1}{\epsilon - H_0} \, V \, \frac{1}{\epsilon - H_0} + \frac{1}{\epsilon - H_0} \, V \, \frac{1}{\epsilon - H_0} \, V \, \frac{1}{\epsilon - H_0} + \cdots$$

where

$$= G_0 + G_0 \ V \ G_0 + G_0 \ V \ G_0 \ V \ G_0 + \cdots \text{ where } G_0 = \frac{1}{e - H_0}$$

letting

$$G = G_0 + G_0 \ V \ G \tag{166}$$

since

$$G_0 + G_0 \ V \ G + G_0 + G_0 \ V \left\{ G_0 + G_0 \ V \right\} \left\{ G_0 + G_0 \ V \ G \right\} \text{ etc} \tag{167}$$

Equation 166 is essentially an integral equation from which the Green function G may in principle be derived.

We are concerned with the scattering problem in which the potential $V(\underline{r})$ is localized. It then becomes important to construct Green's functions that refer to natural casual conditions, with, say, a state $|\psi^+\rangle$ that looks like a simple forward propagating free-space function ϕ at a large distance from the scatterer.

These functions satisfy the integral equation

$$|\psi^+, \underline{r}\rangle = |\emptyset, \underline{r}\rangle + \int G_0^+(\underline{r}, \underline{r}', e) \ V \ (\underline{r}') \ |\psi^+, \underline{r}'\rangle \ d^3\underline{r}' \tag{168}$$

This equation is the representation in real space of the Lippman-Schwinger equation

$$|\psi^+\rangle = |\emptyset\rangle + \frac{1}{e - H_0 + i\delta} \ V \ |\psi^+\rangle \tag{169}$$

The iterative solution of Equation 169 is

$$|\psi^+\rangle = |\emptyset\rangle + \frac{1}{e - H_0 + i\delta} \ V \ |\emptyset\rangle + \frac{1}{e - H_0 + i\delta} V \frac{1}{e - H_0 + i\delta} V \ |\emptyset\rangle + \cdots$$

$$= \left\{ 1 + G_0^+ \ V + G_0^+ \ V \ G_0 \ V + \cdots \right\} |\emptyset\rangle \tag{170}$$

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In the context of the scattering problem, this is called the Born series. The term of nth order in V corresponds to $\underline{n}$ successive virtual scatterings of the particle by the scatterer. To bring this sort of calculation down to earth, let us evaluate the first term. For a plane wave of momentum $\underline{K}$, incident on a localized scatterer, Equation 168 becomes:

$$\psi^+(\underline{r}) = e^{iKr} - \frac{1}{4\pi} \frac{iK|\underline{r}-\underline{r}'|}{|\underline{r}-\underline{r}'|} V(\underline{r}')\psi^+(\underline{r}) \, d^3\underline{r}' \qquad (171)$$

The iterative solution of Equation 171 requires successive integrations over all space. But the first Born approximation, where the unperturbed plane wave is put in place of the true scattered wave under the integral sign can be evaluated. In scattering problems we are only interested in the outgoing wave at a great distance $\underline{r}$ from any part of the region where the scattering potential is appreciable. Asymptotically, we have

$$\frac{e^{iK|\underline{r}-\underline{r}'|}}{|\underline{r}-\underline{r}'|} \rightarrow \frac{e^{iKr}}{r} - \frac{e^{-i(k/r)\underline{r}\cdot\underline{r}'}}{} \quad \text{for } r \gg r'$$

since $|\underline{r}-\underline{r}'| = \sqrt{(r^2 - 2\underline{r}\cdot\underline{r}' + r'^2}} = r\sqrt{1-2\frac{\underline{r}\cdot\underline{r}'}{r^2} - \frac{r'^2}{r^2}}$

$$\approx r\left(1 - \frac{\underline{r}\cdot\underline{r}'}{r^2} - \frac{r'^2}{r^2}\right) \approx r - \left(\frac{\underline{r}}{r}\right)\cdot\underline{r}' \quad \text{or} \quad \frac{e^{iK|\underline{r}-\underline{r}'|}}{|\underline{r}-\underline{r}'|} \approx \frac{e^{iKr-K(\underline{r}/r)\cdot\underline{r}'}}{r}$$

$$= \frac{e^{i\underline{K}\cdot\underline{r}}}{r} \, e^{-i\frac{K}{r}(\underline{r}\cdot\underline{r}')} .$$

The result is then:

$$\psi^+(\underline{r}) \approx e^{i\underline{K}\cdot\underline{r}} - \frac{1}{4\pi} \int \frac{e^{iK|\underline{r}-\underline{r}'|}}{|\underline{r}-\underline{r}'|} V(\underline{r}') e^{i\underline{K}\cdot\underline{r}'} d^3\underline{r}' \tag{172}$$

$$= e^{i\underline{K}\cdot\underline{r}} - \frac{e^{iKr}}{r} \frac{1}{4\pi} \int V(\underline{r}') e^{i(\underline{K}-\underline{K}')\cdot\underline{r}'} d^3\underline{r}' \tag{173}$$

where $\underline{K}'$ is a vector in the direction of r, but having the same magnitude as the incident wave-vector $\underline{K}$.

The term-by-term summation of the Born series is a very inefficient way of calculating transition probabilities, unless the convergence is very rapid. This is not always the case. Almost the only procedure that works is to separate the Schrödinger equation in spherical harmonics and then integrate the radial function outwards to evaluate the phase shift $N_\ell(e)$ for the partial wave of angular momentum ℓ at the energy e.

The exact solution of Equation 171 at large distances is

$$\psi^+(\underline{r}) = e^{i\underline{K}\cdot\underline{r}} + \frac{e^{iKr}}{r} f(\theta) \tag{174}$$

as derived earlier and where

$$f(\theta) = \frac{1}{2iK} \sum_{\ell=0}^{\infty} (2\ell+1)(e^{2iN_\ell}-1)P_\ell(\cos\theta). \tag{175}$$

Comparison with Equation 173 shows that the first term in the Born series is equivalent to making the approximation

$$4\pi f(\theta) \approx - \langle \emptyset_{\underline{K}'} | V | \emptyset_{\underline{K}} \rangle \tag{176}$$

from comparing Equations 175 and 174.

We now deliberately invert this relation, to ask the following question: what operator, t says, gives the exact scattering amplitude

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(Equation 176) for its matrix elements between the free-particle states
$|\phi_K\rangle$ and $|\phi_{K'}\rangle$? We study the same properties of this transition matrix
or t-matrix, which is defined as

$$\langle \phi_{\underline{K}'} |t| \phi_{\underline{K}}\rangle = -4\pi f(\theta) \tag{177}$$

In other words, t is what V would have to become if the Born formula
(Equation 173) were to yield the correct transition probability or:

$$\langle \phi_{\underline{K}'} |t| \phi_{\underline{K}}\rangle = \langle \phi_{\underline{K}'} |V| \psi_{\underline{K}}^+\rangle \tag{178}$$

or

$$t|\phi_{\underline{K}}\rangle = V|\psi_{\underline{K}}^+\rangle \tag{179}$$

Here $|\phi_K\rangle$ represent a free-particle wave function, which acquiring
an outgoing scattered wave when modified into the function $|\psi_{\underline{K}}^+\rangle$.

The significance of the t-matrix is that for the potential scattering
by a spherically symmetrical field, the angular momentum representation
is especially favorable, for the t-matrix is then diagonal. In other
words, Equations 174 and 177 are equivalent to writing for r, r' large
as $t(r, r', \epsilon) = \sum_\ell t_\ell j_\ell (Kr) j_\ell (Kr') Y_{\ell 0}(\hat{r}) Y_{\ell 0}(\hat{r})$ where j_ℓ is a spherical
Bessel function and $Y_{\ell 0}(\hat{r})$ a spherical harmonic for the direction of the
vector r. The diagonal elements of t in this representation are given
by $t_\ell = \frac{1}{2iK}$ (exp 2i $N_\ell(\epsilon) - 1$).

The t-matrix will again appear in the theory of generalized
scattering to follow - so this brief discussion is justified.

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SECTION VIII

MULTIPLE SCATTERING METHOD AS RELEVANT TO THE COMPUTATION

The multiple scattering method, in our case, deals with nonoverlapping spheres, and it includes not only these spheres and the interatomic region between them but also an outer sphere, surrounding the whole molecule, in which the wave function is again expanded in spherical harmonics and radial functions.

The problem we take up is conceptually simple. It is that in which the potential is spherically symmetrical within nonoverlapping atomic spheres, but equal to zero in the space outside these spheres and out to infinity.

The region inside the spheres is designated as Region I, and that outside as Region II. In region II Schrödinger's equation is the ordinary wave equation.

$$\nabla^2 U = -eU \tag{180}$$

or

$$\frac{d^2P}{dr^2} = -[\epsilon - \frac{\ell(\ell+1)}{r^2}]P \tag{181}$$

where

$$U = (\frac{P}{r})Y_{\ell m}(\theta,\emptyset)$$

We are dealing only with negative energies, or bound states of the molecule. The types of solution we wish to use for $\frac{P}{r}$, in spherical coordinates are called $K_\ell^{(1)}$ (Kr) and i_ℓ(Kr) where $K = \sqrt{-\epsilon}$. These functions have forms listed in Appendix B.

These formulas for $K_\ell^{(1)}$ (Kr) include the decreasing exponential, exp(-Kr), so that they all go to zero at infinity. The formulas for i_ℓ(Kr), being regular at the origin, can be expanded in power series in r.

In Region II, which extends out to infinity, we can build up the solution to Schrödinger's equation by superimposing functions of the form $K^{(1)}(Kr)Y_m(\theta,\phi)$ around each nucleus. This function will be bound to go to zero at infinity, and being a linear combination of solutions of Equation 180, all for the same energy, it will be a general solution of that equation, going to zero at infinity. That is, as the general solution in Region II, we may write

$$\psi_{II} = \Sigma(b,\ell,m)A^b_{\ell m}K^{(1)}_\ell(Kr_B)Y_{\ell m}(\hat{r}_B) \tag{182}$$

where B denotes the Bth atom, $|r_B|$ is the distance from the Bth nucleus to the point where the wave function is being computed, and $Y_{\ell m}(\hat{r}_B)$ means the spherical harmonic for the angle of the vector $\hat{r}_B$, using the Bth nucleus as origin. We must now apply the boundary conditions to make this function and the solution in Region I continuous with continuous derivatives over all the spherical surfaces bounding the atomic spheres.

$$U(e,r,\theta,\phi) = \Sigma(\ell m)C_{\ell m}R_{\ell m}(e,r)Y_{\ell m}(\theta,\phi) \tag{183}$$

for the equation

$$\nabla^2 U = -(\epsilon + V)U. \tag{184}$$

Thus, U is a solution of the Schrödinger's equation regular at the origin, containing an infinite number of arbitrary constants, the $C_{\ell m}$'s.

The type of expansion of the wave function (Equation 182) is one possible way of describing it. An alternative form of expansion is, however, more convenient to use in treating the continuity of the wave function over the surface of the spheres. Suppose we wish to expand within a cell containing the particular atom a. There will then be two types of terms in Equation 182; those for which b = a, the functions representing the tail of the atom a, and those for which b ≠ a, representing all the other atoms. We shall expand these tails of atoms b, within the cell a, in terms of r_a and spherical harmonics of the angle $\hat{r}_a$. We employ a result of a general theorem by which we can expand a function of the form $K^{(1)}_\ell(Kr_B)Y_{\ell m}(\hat{r}_B)$ as a linear combination of functions $i_{\ell'}(Kr_a)Y_{\ell'm}(\hat{r}_a)$ around the center a.

Since the function $i_{\ell'}(Kr_a)$ can be expanded in power series as

$$i_{\ell}(Kr) = \frac{(Kr)^{\ell}}{1 \cdot 3 \cdot 5 \cdots (2\ell+1)} \left[1 + \frac{(Kr)^2}{2(2\ell+3)} + \frac{(Kr)^4}{2 \cdot 4 \cdot (2\ell+3)(2\ell+1)} + \cdots \right] \quad (185)$$

and since spherical harmonics $Y_{\ell'm'}(\hat{r}_a)$ can also be expanded in power series in the x,y,z coordinates around nucleus $\underline{a}$, the functions $i_{\ell'}(Kr_a)Y_{\ell m}(\hat{r}_a)$ can also be expanded in x, y and z.

This theorm is (Reference 3)

$$K_{\ell}^{(1)}(Kr_B)Y_{\ell m}(\hat{r}_B) = \underset{\ell'm'L}{\Sigma} \; 4\pi(-1)^{\ell'+1} I_L(\ell'm':\ell m)K_L^{(1)}$$

$$(Kr_{aB})Y_{L,m'-m}^{*}(\hat{r}_{aB}) \quad i_{\ell'}(Kr_a)Y_{\ell'm'}(\hat{r_a}) \quad (186)$$

Here

$$r_{aB} = r_a - r_B \quad (187)$$

and

$$I_L(\ell m;\ell'm') = \int Y_{L,m-m'}(r)Y_{\ell m}^{*}(r)Y_{\ell'm'}(r)d\Omega \quad (188)$$

where the integration is over solid angle.

The integrals over a product of three spherical harmonics are the same ones met in the definition of the Clebsch-Gordon coefficients in the theory of atomic spectra. (They are treated in more detail in the section on generalized scattered-wave theory).

Let us write the whole function ψ_{II} in this form. We then sum over all nuclei $\underline{b}$ except the $\underline{a}$th and include separately the term for nucleus $\underline{a}$.

We have
$$\psi_{II} = \Sigma(b,\ell,m)A_{\ell m}^{B}K_{\ell}^{(1)}(Kr_B)Y_{\ell m}(\hat{r}_B)$$

$$= \underset{\ell m}{\Sigma}\left[A_{\ell m}^{a}K_{\ell}^{(1)}(Kr_a)Y_{\ell m}(\hat{r}_a) + \underset{b\neq a}{\Sigma}\underset{\ell'm'L}{} A_{\ell m}^{B} \; 4\pi(-1)^{\ell'+\ell}\right.$$

$$\left. \times I_L(\ell'm';\ell m)K_L^{(1)}(Kr_{aB})Y_{L,m'-m}^{*}(\hat{r}_{aB})i_{\ell'}(Kr_a)Y_{\ell'm'}(\hat{r}_a)\right] \quad (189)$$

In the second term, we interchange the labels ℓ,m with ℓ',m'. Then we have

$$
\begin{aligned}
\psi_{II} &= \sum_{\ell m} Y_{\ell m}(\hat{r}_a) \left[A^a_{\ell m} K^{(1)}_\ell (K\hat{r}_a) \right. \\
&+ \sum_{B \neq a, \ell'm'L} A^B_{\ell'm'} 4\pi(-1)^{\ell+\ell'} I_L(\ell m; \ell'm') K^{(1)}_L \\
&\quad (K\hat{r}_{aB}) Y^*_{L,m-m'}(\hat{r}_{aB}) \\
&\left. \times i_\ell(Kr'_a) \right] = \sum_{\ell m} Y_{\ell m}(\hat{r}_a) \left[A^a_{\ell m} K^{(1)}_\ell (Kr_a^{\hat{}}) \right. \\
&- \sum_{B \neq a, \ell'm'} K^{-1}_\ell G^{AB}_{\ell m, \ell'm'}(\hat{r}_{aB}) A^B_{\ell'm'} i_\ell(Kr_a) \Big]
\end{aligned}
\tag{190}
$$

where

$$
\begin{aligned}
G^{AB}_{\ell m, \ell'm'}(\hat{r}_{aB}; e) &= (1-\delta_{aB}) 4\pi(-1)^{\ell+\ell'} \sum_L I_L(\ell m; \ell'm') K^{(1)}_L(Kr_{aB}) \\
&\times Y^*_{L,m-m'}(\hat{r}_{aB})
\end{aligned}
\tag{191}
$$

We can rewrite Equation 189 as

$$
\psi_{II} = \sum_{\ell m} Y_{\ell m}(\hat{r}_a) \psi_{II}(\ell m)
$$

where

$$
\psi_{II}(\ell m)
\tag{192}
$$

is the bracket multiplying $Y_{\ell m}(\hat{r}_a)$ in Equation 190.

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We must now produce continuity of the wave function and its first
derivative immediately inside the sphere surround the ath nucleus, where
the wave function is a linear combination of functions $R_\ell(Kr_a)Y_{\ell m}(\hat{r}_a)$,
and immediately outside the sphere, where the function is given by
Equation 189. For continuity of function and derivative at the surface
of the sphere, we make the logarithmic derivative of the term for each ℓ,m
continuous as well as the function ψ itself and its normal derivative.
That is, at the radius of the ath sphere:

$$\frac{1}{\psi_{II}(\ell m)} \frac{d\psi_{II}(\ell m)}{dr_a} = \frac{1}{R_\ell^a(Kr_a)} \frac{dR_\ell^a(Kr_a)}{dr_a} \tag{193}$$

gives

$$\frac{d\psi_{II}(\ell m)}{dr_a} \cdot R_\ell^a(Kr_a) - \psi_{II}(\ell m) \frac{dR_\ell^a}{dr_a}(Kr_a) = 0 \tag{194}$$

If we use bracket notation for the Wronskian, defined as

$$[A(x),B(x)] = A(x)\frac{dB(x)}{dx} - B(x)\frac{dA(x)}{dx} \tag{195}$$

we can rewrite Equation 194 as

$$[R_\ell^a(Kr_a), \psi_{II}(\ell m)] = 0 \tag{196}$$

When we evaluate the Wronskian (Equation 196), we will have at first:

$$\frac{d\psi_{II}(\ell m)}{dr_a} = \sum_{\ell m} A_{\ell m}^a \frac{dK_L^{(1)}}{dr_a}(Kr_a) - \sum_{B\neq a\ell',m'} (-1)^{\ell'}K^{-1}G_{\ell m;\ell'm'}^{aB}$$

$$(\hat{r}_{aB},e) \quad A_{\ell',m'}^B \frac{di_\ell}{dr_a}(Kr_a) \tag{197}$$

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√ This involves terms like $\dfrac{dK_L^{(1)}}{dr_a} \cdot R_\ell^a - \dfrac{di_L}{dr_a} R_a^\ell - K_L^{(1)} \dfrac{dR_\ell^a}{dr_a}$

$+ i_L(Kr_a)\dfrac{dR_\ell^a}{dr_a}$ (neglecting other coefficients not a function of r_a for

simplicity.) This is $\left[\dfrac{dK_L^{(1)}}{dr_a} R_\ell^a - K_L^{(1)}\dfrac{dR_\ell^a}{dr_a}\right] - \left[R_a^\ell \dfrac{di_L}{dr_a} - i_L(Kr_a)\dfrac{dR_\ell^a}{dr_a}\right]$

or $\left[R_\ell^a, K_L^{(1)}\right] - \left[R_a^\ell, i_L(Kr_a)\right]$. Putting this into the total Wron-

skian, we then have:

$$A_{\ell m}^a \left[R_\ell^a, K_\ell^{(1)}(Kr_a)\right] - \sum_{B\neq a,\ell'm'} K^{-1} G_{\ell m,\ell'm'}^a (\hat{r}_{aB};\epsilon)$$

$$\times (-1)^{\ell'} A_{\ell'm'}^B \left[R_\ell^a(Kr_a), i_\ell(Kr_a)\right] = 0 \tag{198}$$

Dividing both terms of Equation 198 by $[R_\ell^a (Kr_a), i_\ell(kr_a)]$, we have

$$A_{\ell m}^a \frac{[R_\ell^a(Kr_a),K_\ell^{(1)}(Kr_a)]}{[R_\ell^a(Kr_a),\, i_\ell(Kr_a)}\tag{199}$$

$$- \sum_{B\neq a,\ell',m'} K^{-1} G_{\ell m,\ell'm'}^{aB} (\hat{r}_{aB};\epsilon)(-1)^\ell A_{\ell',m'}^B = 0$$

where we have such an equation for each $\underline{a}$ (i.e., for each atom), and for each ℓ,m, for which the coefficients $A_{\ell m}^a$ are of appreciable size. Equation 199 gives us the coefficients $A_{\ell m}$ of the wavelets in Region II. We need in addition the coefficients $C_{\ell m}$ of Equation 183 for the expansion inside the atomic spheres. Let us derive the relationship between the A's and C's.

We use Equation 198 to express the summation over b, ℓ, m' which appears in Equation 190 in terms of $A_{\ell m}^a$. We demand that the summations of Equations 190 and 183 representing the solutions inside and outside the $\underline{a}$th sphere, should be equal at the radius r_a of the sphere.

This demands that the coefficients of the spherical harmonics $Y_{\ell m}(\theta,\phi)$ in both summations should be equal for each $\underline{\ell}$ and $\underline{m}$ as well as for each sphere. Then using Equation 199 we have

$$C_{\ell m}^a R_\ell^a(e,r_a) = A_{\ell m}^a K_\ell^{(1)}(Kr_a) - \frac{[R_\ell^a(e,r_a), K_\ell^{(1)}(Kr)]}{[R_\ell^a(e,r_a), i_\ell(Kr_a)]} \quad i_\ell(Kr_a) \tag{200}$$

since

$$i_\ell(Kr)\frac{dK_\ell^{(1)}}{d(Kr)}(Kr) - K_\ell^{(1)}(Kr)\frac{di_\ell(Kr)}{d(Kr)}$$

$$= \left[i_\ell(Kr), K_{\ell(Kr)}^{(1)}\right] = \frac{(-1)^{\ell+1}}{Kr^2} \tag{201}$$

We can reduce Equation 200 as follows:

$$C_{\ell m}^a R^a(e,r_a) = \frac{A_{\ell m}^a K_\ell^{(1)}(Kr_a)\left\{\frac{R^a di_\ell}{dr_a} - i_\ell\frac{dR_\ell^a}{dr_a}\right\}}{[R^a, i_\ell(Kr_a)]}$$

$$- \frac{\left\{R_\ell^a \frac{dK_\ell^{(1)}}{dr_a} - K_\ell^{(1)}\frac{dR_\ell^a}{dR_a}\right\} i_\ell(Kr_a)}{[R_\ell^a, i_\ell(Kr_a)]}$$

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$$= \frac{A_{\ell m}^a \left\{ + K_\ell^{(1)} \frac{di_\ell}{dr_a} - \frac{dK_\ell^{(1)}}{kr_a} i_\ell \right\} R_\ell^a}{[R_\ell^a, i_\ell(Kr_a)]}$$

$$+ \frac{\frac{dR_\ell^a}{dr_a} \left\{ K_\ell^{(1)} i_\ell - K_\ell^{(1)} i_\ell \right\}}{[R_\ell^a, i_\ell(Kr_a)]}$$

$$= \frac{A_{\ell m}^a [K_\ell^{(1)}(Kr_a), i_\ell(Kr_a)] R_\ell^a(e, r_a)}{[R_\ell^a, i_\ell(Kr_a)]}$$

$$= \frac{- A_{\ell m}^a \frac{(-1)^{\ell+1}}{Kr^2}}{[R_\ell^a, i_\ell(Kr_a)]} = C_{\ell m}^a R_\ell^a(e, r_a)$$

or

$$A_{\ell m}^a = C_{\ell m}^a \frac{(Kr_a^2)}{(-1)^\ell} [R_\ell^a, i_\ell(Kr_a)] \tag{202}$$

which is the desired relation between the A's and the C's.

The above equations, and in particular Equation 199, constitute the fundamental equations of the multiple scattering cluster method. The coefficients $A_{\ell m}^B$ determined by these equations are the coefficients of the expansion of the wave function in the interatomic Region II, in terms of the scattered wavelets emitted from each atom. As we have seen, for negative energy these wavelets, instead of being sinusoidal as they would be for positive energy, are falling off exponentially as we go away from the Bth nucleus. We have as many simultaneous linear equations as we have wavelets. In many cases this means that only small value of ℓ need be used because the expansion in scattered wavelets is rapidly convergent. In general the equations will have no solutions, and it is only if the determinant of the coefficients of Equation 191 is zero that we get

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solutions. Since the energy ϵ is entering into the coefficients, we have solutions only for certain energy eigenvalues of the problem, which is the method by which the energy levels are found.

For each eigenvalue, Equation 191 can be solved for the coefficients $A^a_{\ell m}$ and hence for the wave function in Region II. In turn, from Equation 202, we can find the wave function inside each sphere.

SECTION IX

GENERALIZED SCATTERED-WAVE APPROACH TO MOLECULAR-ORBITAL THEORY*

1. INTRODUCTION

This approach is an adoption of a rapidly convergent partial-wave representation of the multicenter wave functions, the use of multiple scattering formalism, and the separation of the principal equations into "structural" and "atomic" quantities. These features distinguish this technique from more conventional LCAO type molecular-orbital methods. This Hamiltonian is based on the partitioning of molecule space into regions of nonoverlapping spherically averaged potential, including a local statistical approximation to the exchange potential. There are no multicenter integrals to compute or to estimate as there are in LCAO methods. The scheme is comparatively easy to implement computationally and is practicable for systems of considerable stereochemical complexity.

2. SOLVING THE INTEGRAL WAVE EQUATION

Consider an N-center molecule having atoms located at the sites R_α ($\alpha = 1,2,...,N$), with respect to some arbitrary origin. In the scattered-wave approach to molecular-orbital theory, we are required to solve the integral Schrödinger equation: (See Appendix C)

$$\psi(\underline{r}) = \int d\underline{r}' G_0(\underline{r},\underline{r}';e)\, V(\underline{r}')\, \psi(\underline{r}') \tag{203}$$

for the stationary states $\psi(\underline{r})$ and energies ε of single electron bound to the local potential field $V(\underline{r})$ of the molecule. $V(\underline{r})$ includes the Hartree-Fock-Slater or X_α statistical approximation to exchange, along with the average Coulomb potential. We assume that the molecular potential at an arbitrary point $\underline{r}$ can be represented as a superposition of overlapping local potentials centered on the atomic sites, namely,

$$V(\underline{r}) = \sum_{\beta=0}^{N} V(\underline{r}-\underline{R_\beta}) \equiv \sum_{\beta=0}^{N} V(\underline{r_\beta}) \tag{204}$$

*This chapter is, in large part, a verbatim synopsis of Reference 11 by K. H. Johnson. This author is gratefully acknowledged.

$G_0(r, r'; \epsilon)$ is the "free-space" single-particle Green's function satisfying the inhomogeneous wave equation.

$$(\nabla^2 + e) \; G_0(\underline{r}, \underline{r}'; e) = \delta(\underline{r} - \underline{r}')' \tag{205}$$

For a polyatomic molecule with overlapping potentials of Equation 204, the integral (Equation 203) cannot be easily solved. However, for the special case of nonoverlapping spherically averaged potentials, we can use Green's theorem to reduce the volume integral in Equation 203 to a sum of surface integrals over spheres, leading to an exactly solvable model.

In order to develop a more flexible class of model potentials for which Equation 203 is still approximately solvable, let us consider the general problem of determining solutions of the integral equation:

$$\psi(\underline{r}) = \int d\underline{r}' \int d\underline{r}'' \; G_0(\underline{r}, \underline{r}''; e) \; U(e; \underline{r}'', \underline{r}') \psi(\underline{r}') \tag{206}$$

for an energy-dependent, non-local potential operator $U(\epsilon; \underline{r}, \underline{r}')$. Equation 206 is solvable provided we expand the potential operator in the separable multicenter partial-wave representation,

$$U(e, \underline{r}, \underline{r}') = \sum_{\beta=1}^{N} \; \sum_{L} \; U_L^{\beta}(e) \; \phi_L(\underline{r}_\beta) \phi_L^*(\underline{r}_\beta') \tag{207}$$

where

$$\phi_L(\underline{r}_\beta) \equiv \phi_L(r_\beta) \; Y_L(\underline{r}_\beta) \tag{208}$$

here $\phi_L(\underline{r}_\beta)$ has been expanded in terms of the product of spherical harmonics $Y_L(\nu,\phi)$ and radial amplitude $\phi_L(r_\beta)$.

Also, in Equations 207 and 208 $L \equiv (\ell,m)$ is the partial-wave (angular momentum) index and $U_L^{\beta}(\epsilon)$ represents certain energy-dependent coefficients; $U_L^{\beta}(\epsilon)$ and $\phi_L(r_\beta)$ are chosen to simulate (exactly or approximately) the originally defined molecular potential (Equation 204) or more general potential configurations. Both may be complex, in general, to allow for the possible use of "optical" or "self-energy" potentials.

Solutions of the integral equation can be generated by substituting Equation 207 into Equation 206 and expanding the Green's function $G_0(\underline{r}, \underline{r}', \epsilon)$ and wavefunction $\psi(\underline{r})$ in the partial-wave representation.

A convenient integral representation of the free-space Green's function is (see Appendix D):

$$G_0(\underline{r}, \underline{r}'; e) = \frac{1}{(2\pi)^3}\, d\underline{q}\, \frac{\exp[r\underline{q} \cdot (\underline{r}-\underline{r}')}{e - q^2} \qquad (209)$$

Because G_0 depends on the difference between "field" and "source" vectors, we can choose to write these vectors with respect to the atomic sites $\underline{R}_\alpha$, namely

$$G_0(\underline{r}_\alpha, \underline{r}'_\beta; e) = \frac{1}{(2\pi)^3}\, \int d\underline{q}\, \frac{\exp[r\underline{q} \cdot (\underline{r}_\alpha - \underline{r}'_\beta - \underline{R}_{\alpha\beta})}{e - q^2}$$

$$\qquad (210)$$

in which

$$\underline{R}_{\alpha\beta} = \underline{R}_\beta - \underline{R}_\alpha$$
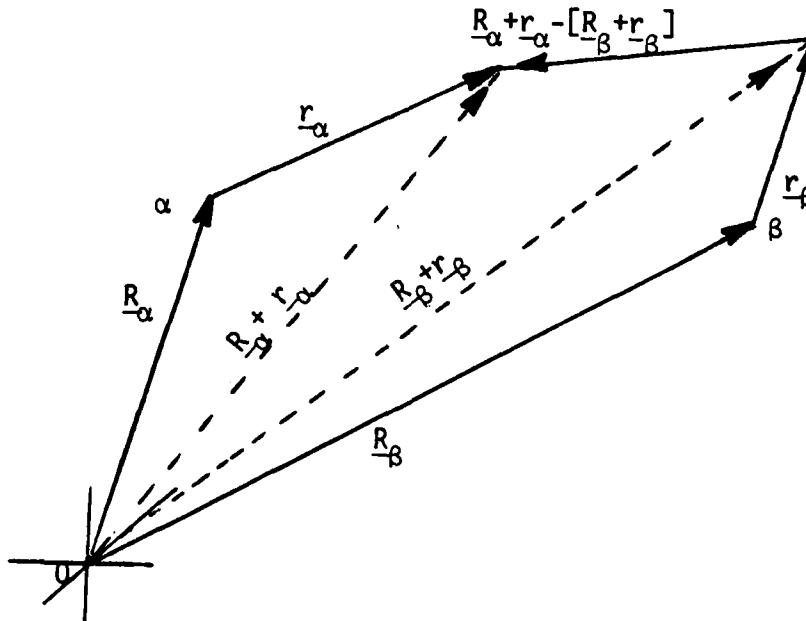
Pictorially, we have

Figure 2.   Diagram Showing Two Potential Points $\underline{r}$ and Two Atomic Sites $\underline{R}$

The vector $\underline{R}_\alpha + \underline{r}_\alpha - [\underline{R}_\beta + \underline{r}_\beta] = \underline{r}_\alpha - r_\beta' - \underline{R}_{\alpha\beta}$ represents the displacement between two arbitrary potential points with respect to two arbitrary atomic sites. We shall use Equation 210 in Equation 206 for those terms in the sum over atomic index β for which $\beta \neq \alpha$. For the case where $\beta = \alpha$, we shall use the alternative representation of G_0, given by (Appendix E)

$$G_0(\underline{r}, \underline{r}'; e) = - \frac{1}{4\pi} \frac{\exp(-K|\underline{r}-\underline{r}'|)}{|\underline{r}-\underline{r}'|}$$

(211)

where for bound states of negative energy $K \equiv \sqrt{-\epsilon}$. The appropriate partial-wave expansions of Equation 211 are

$$G_0(\underline{r}, \underline{r}'; \epsilon) = -K \sum_L (-1)^\ell K_L(K\underline{r}) \, \underline{I}_L^*(K\underline{r}') \quad \text{for } r > r'$$

(212)

$$G_0(\underline{r}, \underline{r}'; \epsilon) = -K \sum_L (-1)^\ell I_L(K\underline{r}) \, K_L^*(K\underline{r}'); \qquad r' > r$$

(213)

In these equations

$$I_L(K\underline{r}) \equiv i_\ell(Kr) Y_L(\underline{r})$$

(214)

$$K_L(K\underline{r}) \equiv K_\ell^{(1)}(Kr) Y_L(\underline{r})$$

(215)

where i_ℓ and $K_\ell^{(1)}$ are modified spherical Bessel and Hankel functions, respectively, defined by

$$i_\ell(x) \equiv i^{-\ell} j_\ell(ix)$$

(216)

$$K_\ell^{(1)}(x) \equiv -i^{-\ell} h_\ell^{(1)}(ix)$$

(217)

These quantities have the advantage that they are real for the negative energies characteristic of bound states. Substituting Equations 207, 210, 212, and 213 into Equation 206 we obtain:

$$\psi(\underline{r}) = \psi(\underline{r}_\alpha + \underline{R}_\alpha) = -K \sum_L (-1)^\ell \left\{ K_L(K\underline{r}_\alpha) \Big|_{r_\alpha' < r_\alpha} \right.$$

$$d\underline{r}_\alpha' \, I_L^*(K\underline{r}_\alpha') \sum_{L'} \phi_{L'}(\underline{r}_\alpha')$$

$$\left. + I_L(K\underline{r}_\alpha) \int_{r_\alpha' > r_\alpha} d\underline{r}_\alpha' \, K_L^*(K\underline{r}_\alpha') \sum_{L'} \phi_{L'}(\underline{r}_\alpha') \right\}$$

$$U_{L'}^\alpha(\underline{e}) \int d\underline{r}_\alpha'' \, \phi_{L'}^*(\underline{r}_\alpha'') \, \psi(\underline{r}_\alpha'' + \underline{R}_\alpha)$$

$$+ \frac{1}{(2\pi)^3} \int d\underline{q} \, \exp(i\underline{q}\cdot\underline{r}_\beta) \sum_{\substack{\beta \neq \alpha}}^N \frac{\exp(-i\underline{q}\cdot\underline{R}_{\alpha\beta})}{\epsilon - q^2}$$

$$\times \int d\underline{r}_\beta' \, \exp(-i\underline{q}\cdot\underline{r}_\beta') \sum_{L'} \phi_{L'}(\underline{r}_\beta') U_{L'}^\beta(\epsilon)$$

$$\int d\underline{r}_\beta'' \, \phi_{L'}^*(\underline{r}_\beta'') \, \psi(\underline{r}_\beta'' + \underline{R}_\beta)$$

(218)

We then expand $\psi(\underline{r}_\alpha + \underline{R}_\alpha)$ in the partial-wave representation:

$$\psi(\underline{r}_\alpha + \underline{R}_\alpha) = \sum_L C_L^\alpha R_L^\alpha(r_\alpha) Y_L(\underline{r}_\alpha) \tag{219}$$

where the $R_L^\alpha(r_\alpha)$ are unknown radial amplitudes for the one-electron orbitals and $Y_L(\underline{r}_\alpha)$ are spherical harmonics.

We next expand the plane waves in terms of radial functions (Bessel functions) and spherical harmonics so that the angular functions are all expanded in terms of the same basis functions, namely, the spherical harmonics. Since it has already been shown that plane waves can be expanded in terms of analytic Bessel functions explictly as well, this

presents no problem; however, one must bear in mind that the wave function $\psi(\underline{r}_\alpha + \underline{R}_\alpha)$ is _not_ an explicit analytic function of a radial coordinate, such as a Bessel function, but rather is a more complicated radially dependent function to be determined.

Expanding the plane waves,

$$\exp(i\underline{q} \cdot \underline{r}_\alpha) = 4\pi \sum_L i^\ell j_\ell(qr_\alpha) Y_L^*(\underline{q}) Y_L(\underline{r}_\alpha) \tag{220}$$

$$\exp(-i\underline{q} \cdot \underline{r'}_\beta) = 4\pi \sum_L i^{-\ell} j_\ell(qr'_\beta) Y_L(\underline{q}) Y_L^*(\underline{r'}_\beta) \tag{221}$$

and using Equations 208, 214, 215, and 219 through 221 in Equation 218 we have:

$$\psi(\underline{r}) = \psi(\underline{r}_\alpha + \underline{R}_\alpha) = \sum_L C_L^\alpha R_L^\alpha(r_\alpha) Y_L(\underline{r}_\alpha) \tag{222}$$

$$= -K \sum_L (-1)^\ell \left\{ K_\ell^{(1)}(Kr_\alpha) Y_L(\underline{r}_\alpha) \int_{r'_\alpha < r_\alpha} d\underline{r'}_\alpha \right.$$

$$i_\ell(Kr'_\alpha) Y_{(\underline{r'}_\alpha)}^* \sum_{L'} \phi_L'(r'_\alpha)$$

$$\times Y_L'(\underline{r'}_\alpha) + i_\ell(Kr_\alpha) Y_L(\underline{r}_\alpha) \int_{r'_\alpha > r_\alpha} d\underline{r'}_\alpha K_\ell^{(1)}(Kr'_\alpha) Y_L^*(\underline{r'}_\alpha)$$

$$\times \left. \sum_{L'} \phi_L'(r'_\alpha) Y_{L'}(\underline{r'}_\alpha) \right\} U_{L'}^\alpha(e) \int dr''_\alpha \phi_{L'}(r''_\alpha) Y_{L'}^*(\underline{r''}_\alpha)$$

$$\sum_L C_L^\alpha R_L^\alpha(r''_\alpha) Y_L(r''_\alpha)$$

$$+ \frac{1}{(2\pi)^3} \int d\underline{q} \cdot 4\pi \sum_L i^\ell j_\ell(qr_\alpha) Y_L^*(\underline{q}) Y_L(\underline{r}_\alpha) \sum_{\beta \neq \alpha}^N \frac{\exp(-i\underline{q} \cdot \underline{R}_{\alpha\beta})}{e - q^2}$$

$$\times \int d\underline{r'}_\beta \cdot 4\pi \sum_{L'} i^{-\ell'} j_\ell(qr'_\beta) Y_{L'}(\underline{q}) Y_{L'}^*(\underline{r'}_\beta) \sum_{L'} \phi_L'(\underline{r'}_\beta)$$

$$\times Y_{L'}(\underline{r'}_\beta) U_{L'}^\beta(e)$$

$$\times \sum_{L'} \int dr''_{\beta} \; \phi_{L'}(r''_{\beta}) \; Y^*_{L'}\underbrace{(r''_{\beta})} \sum_{L} C^{\beta}_{L} \; R^{\beta}_{L'}(r''_{\beta}) \; Y_{L'}\underbrace{(r''_{\beta})}$$

From the orthonormality of spherical harmonics, we see immediately that the functions under which brackets ⌣ appear can be integrated over solid angle $d\Omega$ as $\int d\Omega(\underline{r}) \; Y^*_L(\underline{r}) \; Y_{L'}(r) = \delta_{LL'}$, remembering of course that

$$\int dr'_{\alpha} \int_0^{\infty} \int_0^{\pi} \int_0^{2\pi} d\phi'_{\alpha} \; d\theta'_{\alpha} \; \sin\theta'_{\alpha} \; dr_{\alpha} r'^2_{\alpha}$$

Integrating with respect to the spherical harmonics, we have

$$\psi(\underline{r}) = \sum_L C^{\alpha}_L \; R^{\alpha}_L(r_{\alpha}) \; Y_L(\underline{r}_{\alpha}) = -K \sum_L (-1)^{\ell} \Big\{ K^{(1)}_{\ell}(Kr_{\alpha}) \; Y_L(\underline{r}_{\alpha})$$

$$\times \int_{r'_{\alpha} < r_{\alpha}} dr'_{\alpha} \; r'^2_{\alpha} \; i_{\ell}(Kr'_{\alpha}) \; \phi_L(r'_{\alpha}) + i_{\ell}(Kr_{\alpha}) \; Y_L(\underline{r}_{\alpha})$$

$$\times \int_{r'_{\alpha} > r_{\alpha}} dr'_{\alpha} \; r'^2_{\alpha} \; K^{(1)}_{\ell}(kr'_{\alpha}) \; \phi_L(r'_{\alpha}) \Big\} U^{\alpha}_L(\epsilon) \int_0^{\infty} dr''_{\alpha} \; r''^2_{\alpha} \; \phi^*_L(r''_{\alpha}) C\alpha_L R^{\alpha}_L(r''_{\alpha})$$

$$+ \frac{1}{(2\pi)^3} \int d\underline{q} \cdot 4\pi \sum_L i^{\ell} j_{\ell}(qr_{\alpha}) \; Y^*_L(\underline{q}) \sum_{\beta \neq \alpha}^{N} \frac{\exp(-i\underline{q} \cdot \underline{R}_{\alpha\beta})}{e-q^2}$$

$$\times \; Y_L(\underline{r}_{\alpha})$$

$$\times \int_0^{\infty} dr'_{\beta} \; r'^2_{\beta} \sum_{L'} i^{-\ell'} j_{\ell}(qr'_{\beta}) \; Y_{L'}(\underline{q}) \; \phi_{L'}(r'_{\beta}) \; U^{\beta}_{L'}(\epsilon) \int dr''_{\beta} \; r''^2_{\beta}$$

$$\times \; \phi^*_{L'}(r''_{\beta}) \; C^{\beta}_{L'} \; R^{\beta}_{L'}(r''_{\beta})$$

Looking at the Lth component and dividing $Y_L(\underline{r}_\alpha)$ out from both sides of this equation, we have:

$$C_L^\alpha\, R_L^\alpha(r_\alpha) = K \sum_L (-1)^{\ell+1} \left\{ K_\ell^{(1)}(Kr_\alpha) \int_{r_\alpha' < r_\alpha}^{r_\alpha} r_\alpha'^2\, dr_\alpha'\, i_\ell(Kr_\alpha')\phi_L(r_\alpha') \right.$$

$$\left. + i_\ell(Kr_\alpha) \int_{\substack{r_\alpha \\ r_\alpha' > r_\alpha}}^{\infty} r_\alpha'^2\, dr_\alpha'\, K_\ell^{(1)}(Kr_\alpha')\, \phi_L(r_\alpha') \right\} C_L^\alpha U_L^\alpha(e)$$

$$\times \int_0^\infty r_\alpha''^2\, dr_\alpha''\, \phi_L^*(r_\alpha'')\, R_L^\alpha(r_\alpha'') + \frac{2}{\pi}\, i^\ell \int dq\, j_\ell(qr_\alpha)\, Y_L^*(\underline{q})$$

$$\times \sum_{\beta \neq \alpha}^{N} \frac{\exp(-i\underline{q}\cdot\underline{R}_{\alpha\beta})}{e-q^2} \sum_{L'} i^{-\ell'} \int_0^\infty r_\beta'^2\, dr_\beta'\, j_{\ell'}(qr_\beta')\phi_{L'}(r_\beta')Y_{L'}(\underline{q})$$

$$\times C_{L'}^\beta\, U_{L'}^\beta(e) \int_0^\infty r_\beta''^2\, dr_\beta''\, \phi_{L'}^*(r_\beta'')\, R_{L'}^\beta(r_\beta'')$$

This rather complicated looking expression can be simplified, and the terms can be given a physical interpretation. First, we expand the plane wave,

$$\exp(-i\underline{q}\cdot\underline{R}_{\alpha\beta}) = 4\pi \sum_{L''} i^{-\ell''} j_{\ell''}(qR_{\alpha\beta})\, Y_{L''}(\underline{q})\, Y_{L''}^*(\underline{R}_{\alpha\beta}) \qquad (223)$$

Inserting this into the corresponding part of Equation 222, we have

$$\frac{2}{\pi}\, i^\ell \int d\underline{q}\, j_\ell(qr_\alpha)\, \underline{Y_L^*(\underline{q})}\, \sum_{\beta \neq \alpha}^{N} 4\pi \sum_{L''} i^{-\ell''} j_{\ell''}(qR_{\alpha\beta})\underline{Y_{L''}(\underline{q})}$$

$$\times Y_{L''}^*(\underline{R}_{\alpha\beta})$$

$$\times \sum_{L'} i^{-\ell'} \int_0^\infty r_\beta'^2\, dr_\beta'\, j_{\ell'}(q r_\beta')\, \phi_{L'}(r_\beta')\, \underline{Y_{L'}(\underline{q})}$$

$$\times \cdots$$

$$\Rightarrow \int d\Omega(\underline{q})\, Y_{L''}(\underline{q})\, Y_L^*(\underline{q})\, Y_{L'}(\underline{q}) \equiv \frac{T}{\ell''}(L;L')$$

These are the Gaunt integrals, which are non-zero only for $|\ell - \ell'| \leq \ell'' \leq \ell + \ell'$ and $\ell + \ell' + \ell'' =$ even integer.

The Gaunt integrals can be expressed as products of Clebsch-Gordon coefficients, and tabulations of them are readily available. Using the notation

$$A_L^\alpha(e) \equiv C_L^\alpha \, U_L^\alpha(\epsilon) \int_0^\infty r_\alpha^2 dr_\alpha \phi_L^*(r_\alpha) R_L^\alpha(r_\alpha) \tag{224}$$

$$\phi_L^\alpha(q) \equiv \int_0^\infty r_\alpha^2 \, dr_\alpha j_\ell(qr_\alpha) \, \phi_L(r_\alpha) \tag{225}$$

$$f_L(r_\alpha;e) \equiv K(-1)^{\ell+1} \int_0^{r_\alpha} r_\alpha'^2 \, dr_\alpha' \, i_\ell(Kr_\alpha') \, \phi_L(r_\alpha') \tag{226}$$

$$g_L(r_\alpha;e) \equiv K(-1)^{\ell+1} \int_{r_\alpha}^\infty r_\alpha'^2 \, dr_\alpha' K_\ell^{(1)}(Kr_\alpha') \, \phi_L(r_\alpha') \tag{227}$$

$$G_{L'L}^{\alpha\beta}(R_{\alpha\beta};q) \equiv 4\pi i^{\ell-\ell'} q \sum_{L''} i^{-\ell''} I_{L''}(L;L') j_{\ell''}(qR_{\alpha\beta}) Y_{L''}^*(R_{\alpha\beta} \tag{228}$$

we arrive at the equation

$$C_L^\alpha R_L^\alpha(r_\alpha) = A_L^\alpha(e)[f_L(r_\alpha;e)K_\ell^{(1)}(Kr_\alpha) + g_L(r_\alpha;e)i_\ell(Kr_\alpha)]$$

$$+ \frac{2}{\pi} \sum_{\beta \neq \alpha}^N \sum_{L'} A_L^\beta(\epsilon) \int_0^\infty q \, dq j_\ell(qr_\alpha)(e-q^2)^{-1}$$

$$G_{LL'}^{\alpha\beta}(R_{\alpha\beta};q) \, \phi_{L'}^\beta(q) \, . \tag{229}$$

Since all the quantities of Equations 223 through 228 are known, the radial functions $C_L^\alpha R_L^\alpha$ (and hence the effective single-particle wavefunctions) can be determined, once the coefficients A_L^α (Equation 224) are calculated. To determine the A_L^α and the single-particle energies, we multiply Equation 229 by $r_\alpha^2 \phi_L^*(r_\alpha)$ and integrate over all r_α. Using Equation 225 and collecting terms, we obtain

$$\sum_{\beta=1}^N \sum_{L'} \left| \delta_{\alpha\beta}\delta_{LL'} \left[U_L^\alpha(e)^{-1} - \int_0^\infty r_\alpha^2 dr_\alpha \phi_L^*(r_\alpha) f_L(r_\alpha;e) K_\ell^{(1)}(Kr_\alpha) \right. \right. \tag{230}$$

$$- \int_0^\infty r_\alpha^2 dr_\alpha \phi_L^*(r_\alpha) g_L(r_\alpha;e) i_\ell(Kr_\alpha) \Big]$$

$$\left. - (1-\delta_{\alpha\beta})\frac{2}{\pi}\int_0^\infty q\, dq \phi_L^{\alpha*}(q)(e-q^2)^{-1} G_{LL'}^{\alpha\beta}(\underline{R}_{\alpha\beta};q)\phi_{L'}^\beta(q) \right] A_L^\beta(e) = 0$$

This is a set of linear, homogeneous equations in the coefficients A_L^β. To give some physical significance to the matrix elements in Equation 230 we divide each row α by the quantity

$$\phi_L^{\alpha*}(e) \equiv \int_0^\infty r_\alpha^2 dr_\alpha i_\ell(Kr_\alpha)\phi_L^*(r_\alpha) \tag{231}$$

and each column β by the quantity

$$\phi_{L'}^\beta(e) \equiv \int_0^\infty r_\beta^2 dr_\beta i_{\ell'}(Kr_\beta)\phi_{L'}(r_\beta) \tag{232}$$

Then we can write Equation 230 in the form

$$\phi_L^{\alpha*}(e) \sum_{\beta=1}^N \sum_{L'} \left\{ \delta_{\alpha\beta}\delta_{LL'}[t_L^\beta(e)]^{-1} - G_{LL'}^{\alpha\beta}(R_{\alpha\beta};e) \right\} A_{L'}^\beta(e) \tag{233}$$

$$\times \phi_{L'}^\beta(e) = 0$$

in which we have introduced the notation

$$t_L(\epsilon) \equiv \qquad\qquad\qquad\qquad (234)$$

$$\frac{\phi_L^{\alpha*}(\epsilon)\phi_L^{\alpha}(\epsilon)}{[U_L^{\alpha}(\epsilon)]^{-1} - \int_0^\infty r^2 dr_\alpha \phi_L^*(r_\alpha)[f_L(r_\alpha;\epsilon)K_\ell^{(1)}(Kr_\alpha) + g_L(r_\alpha;\epsilon)i_\ell(Kr_\alpha)]}$$

$$G_{LL'}(\underline{R}_{\alpha\beta};\epsilon) \equiv (1 - \delta_{\alpha\beta}) \frac{2}{\pi} [\phi_L^{\alpha*}(\epsilon)\phi_{L'}^{\beta}(\epsilon)]^{-1}$$

$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (235)$$

$$\times \int_0^\infty q \, dq \phi_L^{\alpha*}(q)(\epsilon - q^2)^{-1} G_{LL'}^{\alpha\beta}(\underline{R}_{\alpha\beta};q)\phi_{L'}^{\beta}(q)$$

The bound-state, single-particle energies correspond to zeros of the secular determinant (Appendix H).

$$|\delta_{\alpha\beta} \quad \delta_{LL'} \cdot [t_L^{\beta}(\epsilon)]^{-1} - G_{LL'}^{\alpha\beta}(R_{\alpha\beta};\epsilon) \qquad\qquad (236)$$

One can solve for the coefficients $A_L^{\beta}(\epsilon)$ corresponding to these energies via Equation 233 and then for the effective single-particle orbitals by Equation 229.

DISCUSSION OF THE COMPUTER PROGRAMS

1. HSRHF ATOMIC PROGRAM

The program of F. Herman and S. Skillman (Reference 5) for the self-consistent-field Hartree-Fock-Slater calculations on atoms, has been modified to allow for variable alpha in the X-alpha approximation to exchange correlation.

The object of this program is to obtain a self-consistent solution of non-relativistic Hartree-Fock-Slater equations for a free atom or ion, given the atomic number Z, the electronic configuration (which is specified by the orbital configuration numbers) and the self-consistency criterion β (SCF).

The input information includes a trial or starting potential, a set of trial energy eigenvalues, as well as other information. The solution includes the self-consistent potential expressed in the form $[rV(r)]$; the energy eigenvalues E_n and the normalized radial wave functions $P_{n\lambda}(r)$ at all (or some) of the 441 points of the integration mesh and the values of $P_{n\lambda}(r)/_r\lambda+1$ ar $r = 0$. This information is expressed in floating point form to eight significant figures.

Some of the data required includes Schwarz's alpha parameter, Green's parameter for generating the potential, and trial energy values. The latter are obtained from Reference 5.

The calculated free-atom eigenvalues and charge densities are input to the potential-superposition-program MOLPOT (Molecular Potential).

2. MOLPOT

MOLPOT is used to construct the initial molecular potential for X-alpha standing wave calculations, by superposition of free-atom potentials and spherical averaging of the superposition in each atomic

and the extramolecular region. Free-atom potentials are calculated from the input HSRHF charge densities, the Coulomb term being obtained from Poisson's equation and the exchange term from Slater's X-alpha approximation.

Various calculations are required as input data for MOLPOT. For instance, the α parameter for the interatomic region is needed. This is usually a weighted average of the atomic α's; possible choices for the weights are the atomic sphere volumes or numbers of electrons per atom. The HSRHF charge densities, one for each unique atom, are required; coordinates of each atom with respect to a symmetry center or other geometrical origin must also be provided. This calculation can be involved, depending on the complexity of the molecule. At times, a physical model of the complex can facilitate geometrical insight into the relative positions of atoms, nearest neighbors, etc.

MOLPOT provides the free-atom potential, charge density, and integrated charge $\rho_{r_0} = \int_{r_0}^{r_0} 4\pi r^2 \rho(r)dr$, printed as a function of $\underline{r}$ for each unique atom prior to the potential superposition. After superposition, the quantities r, $V(r)$, $rV_c(r)$, $V_{r_0}\rho(r)$, and ρ_{r_0} are tabulated.

3. HARMONY

HARMONY calculates the spherical harmonic basis functions for a given symmetry, range of $\underline{\ell}$ values, and arrangement of atoms, by a projection operator approach.

Representations of a given molecular point group including inversion must be included in the input. The basis functions which are generated are then orthogonalized. This output is punched in the proper format for input to the Energy and SCF programs (see below). The calculations are made for each representation for each group of equivalent atoms in the molecule which have different angular relations to each other.

4. ENERGY

The program, ENERGY, is the non-self consistent version of the main X-αSW program. The program searches for eigenvalues within specified energy ranges for an input molecular potential and symmetry. It is most commonly employed to obtain initial energy levels to start the SCF process, and to convert the long-form molecular potential from MOLPOT to the short form used as input to the SCF program.

It is used to search for excited states at self-consistency, or to obtain radial wave functions and their coefficients for input to the contour-mapping program.

Input data include radii of atomic spheres (including the outer sphere), the basis functions for a particular representation (from HARMONY), and the energy range of valence levels.

The output from ENERGY consists of (1) the input potential in each region, always converted to the short form in print, and if desired in punch, and (2) for each representation, the input symmetry and a table of energy values, determinant values, and Ramsauer factors in the specified energy ranges, with indicated determinant zeros.

The Ramsauer factor, always +1 or -1, is included since the program will occasionally indicate a zero due to a change in its sign, when in fact the determinant has not changed sign, the latter being the criterion for a true zero.

5. SCF

The self-consistent version of the main X-alpha SW program searches for eigenvalues at $E_i \pm \Delta E_i$, where E_i and ΔE_i are specified for each state $\underline{i}$, and $\underline{n}$ takes on the values 1, 2, 3, etc. until a determinant zero is found. It calculates normalized probability densities $\int \psi_i^* \psi_i$ in the various regions for each state $\underline{i}$. After all states have been calculated, occupation numbers are assigned according to input criteria, and a new many-electron charge density and potential, as well as total and kinetic energies, are obtained. The new potential is then normally

used as input for another iteration until the eigenvalues converge to
$\pm$ 0.001 Rydbergs.

Input data include energy eigenvalues of each shell for each atomic
representation, the HARMONY output deck, and the potential deck from
MOLPOT.

Printed output from SCF consists of the input potential and symmetry,
followed by the eigenvalue determination, normalization factor, and
normalized probability densities in the various region for each state.
At the end of each iteration the eigenvalues and probabilities are
summarized along with the total and kinetic energies, the various
components of the total potential energy, the total charge in each
region, the largest fractional difference between the old and new
potential, and the new potential itself.

SECTION XI

THE CALCULATION

1. STATEMENT OF THE PROBLEM

The cluster complex to be calculated is C_5H_9. The energy eigenvalues shall be calculated and compared with those of C_5H_{12} obtained by Watkins and Messmer (Reference 28). This intercomparison will determine whether the lowered symmetry of C_5H_9 (C_{3v} symmetry) shifts the eigenvalues of the more symmetrical cluster C_5H_{12} (T_d symmetry). Physically, if the eigenvalues are shifted, it may happen that the bulk states at the top of the valence band of diamond will split away, forming a surface state within the gap. This state, if it exists, must be associated with the three missing hydrogen atoms i.e., with the three dangling bonds at the (111) surface.

If the state exists, the calculation will determine its location relative to the top of the valence band, that is, that energy required to excite an electron from the top of the valence band into the surface state.

2. INPUT CALCULATIONS

Certain calculations are required as input data to the programs. These include the tetrahedral geometry, coordinates of atoms, symmetry point group analysis, and atomic and outer sphere radii.

3. THE DIAMOND STRUCTURE (REFERENCE 31)

The space lattice of diamond is face-centered cubic. A primitive basis of two identical atoms 000; 1/4 1/4 1/4 is associated with each lattice point, as shown in Figure 3(a). The tetrahedral bonding of the diamond structure is represented in Figure 3(b). Each atom has four nearest neighbors and 12 second-nearest neighbors. Here are eight atoms in a unit cube. The diamond structure is the result of fourfold directional covalent bonding.
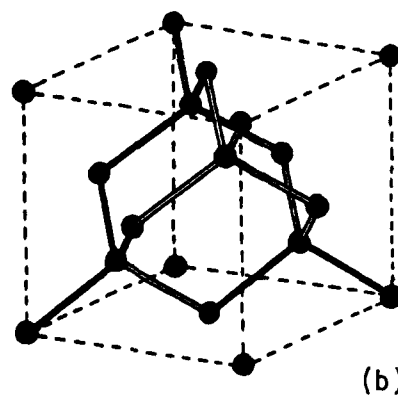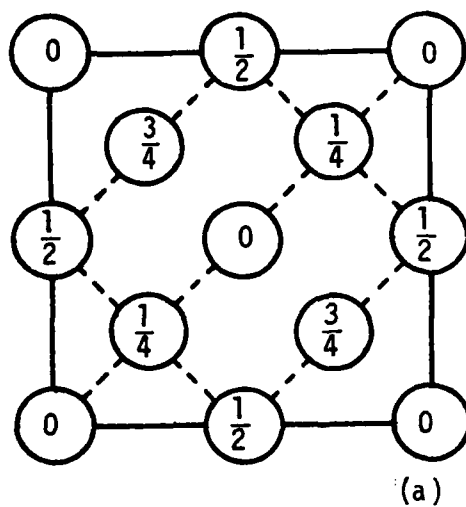
(a)

(b)

Figure 3. Diamond Structure

4. The C_5H_9 STRUCTURE

In the C_5H_9 structure there is a carbon atom at the center of the tetrahedron formed by its four nearest neighbors. The 12 second-nearest neighbors can be subdivided into four groups of three atoms each, each group lying in a plane parallel to one of the four faces of the tetrahedron. If one of these groups is removed, the corresponding face represents the unrelaxed, unreconstructed (111) diamond surface. The remaining nine second-nearest neighbors are replaced by hydrogen atoms to tie up the dangling bonds, resulting in a C_5H_9 structure with C_{3v} symmetry. This structure is shown in Figure 4, where the basal plane represents the (111) surface and the dashed lines represent the three dangling surface bonds. In the numbering scheme used in the calculations, the carbon atoms are numbered 3, 4, 5, 8 and 9, and the hydrogen atoms are 6, 7 and 10 through 16. "Atom" 1 denotes an outer sphere, concentric with atom 3, large enough to encompass the cluster, and "atom" 2 denotes a missing H atom absorbed on the (111) surface just below the center of the basal plane. This "vacancy" atom is included for comparison with future studies of hydrogen absorption on diamond. With respect to the coordinate axes shown in Figure 4, the coordinates of the atomic spheres used in the calculation is given in Table 1, both in units of $a_0/4$ and in atomic units (au), where $a_0 = 3.566$ Å $= 6.7387$ au is the length of the cube edge in the diamond lattice (at 0 K) and 1 au $= 0.52918$ Å. The coordinates of the vacancy are determined assuming it just touches the center carbon atom.

5. SYMMETRY POINT-GROUP ANALYSIS

The symmetry point group of C_5H_9 is C_{3v}. Rotation about the basal plane of the cluster is in 120° steps, such that the identity matrix is generated at $(C_3)^3$.

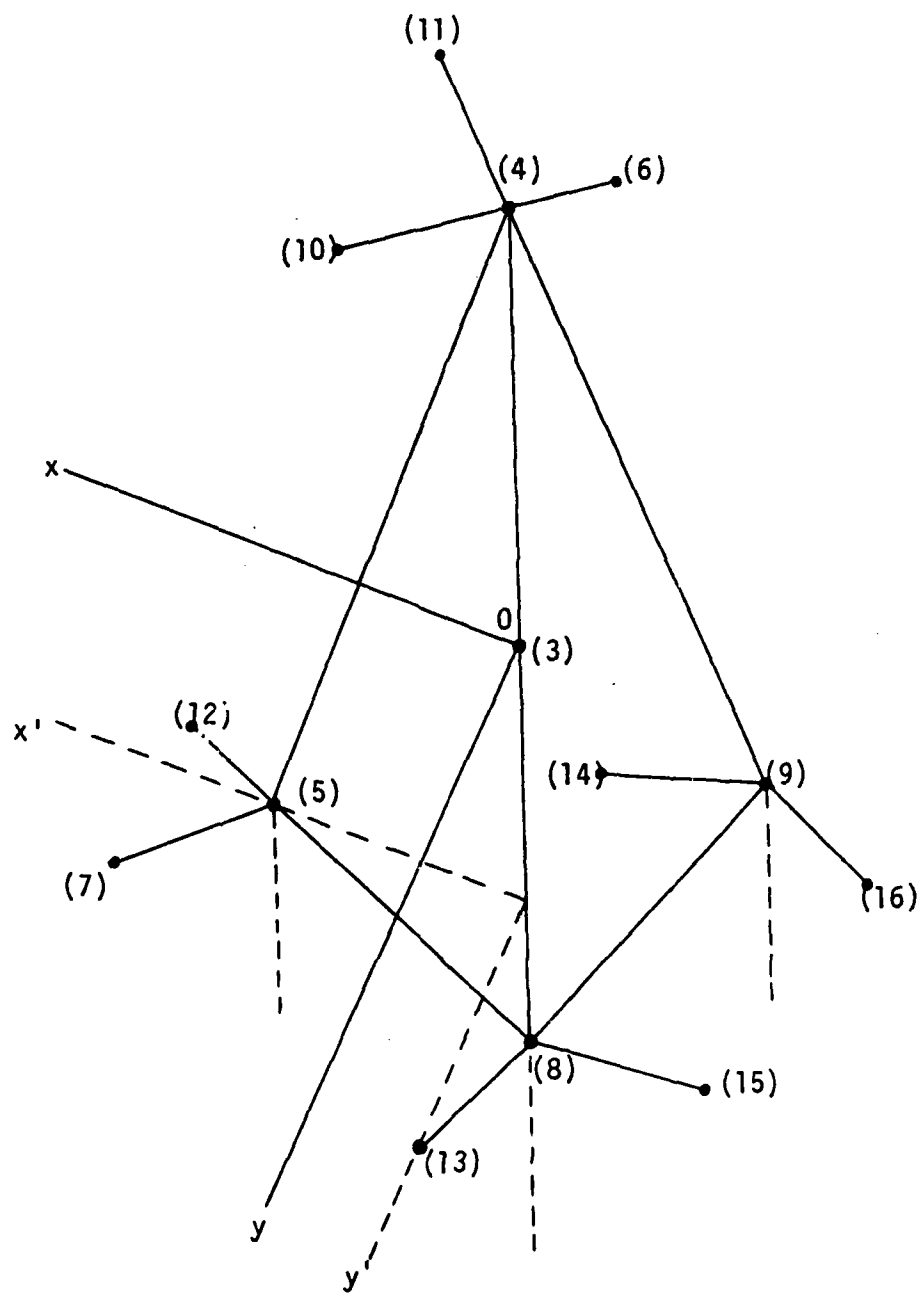In order to see this, the rotation of axes about an arbitrary angle in the x-y plane is shown in Figure 5.

Figure 4.   Geometry of the C$_5$H$_9$ Cluster, Showing, by Atom
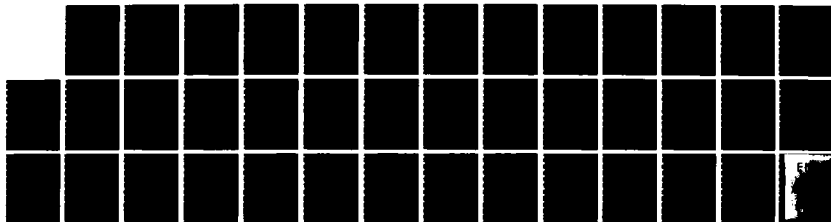Numbers, the Locations of the Atomic Center

MICROCOPY RESOLUTION TEST CHART
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TABLE COORDINATES OF THE ATOMIC SPHERES OF THE C_5H_9 CLUSTER

| ATOM	(x,y,z) (units of $a_0/4$)	(x,y,z) (au)
3(carbon)	$(0,0,0)$	$(0,0,0)$
4(carbon)	$(0,0,\sqrt{3})$	$(0, 0, 2.9179546)$
5(carbon)	$(\sqrt{8}/3, 0, -\sqrt{1}/3)$	$(2.751074, 0, -0.9726516)$
8(carbon)	$(-\sqrt{2}/3, \sqrt{2}, -\sqrt{1}/3)$	$(-1.375537, 2.38250, -0.9726516)$
9(carbon)	$(-\sqrt{2}/3, -\sqrt{2}, -\sqrt{1}/3)$	$(-1.375537, -2.38250, -0.9726516)$
6(hydrogen)	$(-\sqrt{8}/3, 0, \sqrt{16}/3)$	$(-2.751074, 0, 3.8906062)$
7(hydrogen)	$(\sqrt{6}, \sqrt{2}, 0)$	$(4.1266109, 2.38250, 0)$
10(hydrogen)	$(\sqrt{2}/3, \sqrt{2}, \sqrt{16}/3)$	$(1.375537, 2.38250, 3.8906062)$
11(hydrogen)	$(\sqrt{2}/3, -\sqrt{2}, \sqrt{16}/3)$	$(1.375537, -2.38250, 3.8906062)$
12(hydrogen)	$(\sqrt{6}, -\sqrt{2}, 0)$	$(4.1266109, -2.38250, 0)$
13(hydrogen)	$(0, \sqrt{8}, 0)$	$(0, 4.7649999, 0)$
14(hydrogen)	$(0, -\sqrt{8}, 0)$	$(0, -4.7649999, 0)$
15(hydrogen)	$(-\sqrt{6}, \sqrt{2}, 0)$	$(-4.1266109, 2.38250, 0)$
16(hydrogen)	$(-\sqrt{6}, -\sqrt{2}, 0)$	$(-4.1266109, -2.38250, 0)$
1(outer sphere)	$(0,0,0)$	$(0,0,0)$
2(vacancy sphere)	$(0, 0, -1.2819534)$	$(0, 0, -2.1596840)$
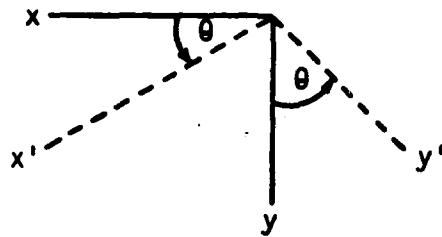
Figure 5. Rotation of Axes in the x-y Plane

$$x' = x \cos \theta + y \cos \left(\frac{\pi}{2} - \theta\right)$$

$$x' = x \cos \theta + y \sin \theta$$

$$y' = x \cos\left(\frac{\pi}{2} + \theta\right) + y \cos \theta$$

$$y' = -x \sin \theta + y \cos \theta$$

$$\begin{aligned} x' \\ y' \end{aligned} = \begin{pmatrix} \cos \theta & \sin \theta \\ -\sin \theta & \cos \theta \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}$$

The matrices for C_3, C_3^2, and C_3^3 are given below. Furthermore, as can be seen from Figure 6, triangular symmetry of the basal planes also evokes reflections depicted by the σ-axes. σ_5 maps position seven into position six, and vice versa. σ_6 maps position five into position seven and vice versa which σ_7 maps position five into position six and vice versa. These operations generate additional symmetry to C_{3v}. The σ operations may also be construed as permutations and illustrative matrices are included. Further note that $\sigma_6 = \sigma_5 C_3^2$, that is, σ_6 can be generated by rotating the system 240 degrees, then applying σ_5 operation. This is similar for σ_7 as well since $\sigma_7 = \sigma_5 C_3$.

6. OTHER INPUT PARAMETERS

The radii of the atomic spheres were determined by assuming touching spheres, resulting in a radius for atoms 3 through 16 of one-half the nearest-neighbor distance in diamond, or 1.4589773 au. The vacancy sphere was assigned a radius equal to one-half the bond distance in the ground state of the H_2 molecule, or 0.7007067 au. The outer sphere radius was taken as the smallest possible for encompassing all the atoms, or 6.2239775 au.

The values of the exchange parameter, $\underline{\alpha}$, were taken as $\alpha_c = 0.75928$ for carbon and $\alpha_H = 0.97804$ for hydrogen, from the compilation by Schwarz (Reference 19). For the inter-atomic region, α was determined by weighting α_c and α_H with the number of valence electrons (4 per C atom and 1 per H atom), giving $\alpha_{int} = 0.82661$.

The maximum value of ℓ in the partial-wave expansion of the symmetrized basis functions was $\ell = 1$ for functions constructed from the hydrogen orbitals and $\ell = 2$ for functions constructed from the carbon orbitals.

The fraction of the new potential used in each iteration was 0.1. No spin polarization was assumed, and the self-consistency criterion was a 1% variation in the potential between successive iterations, up to a maximum of 50 iterations.
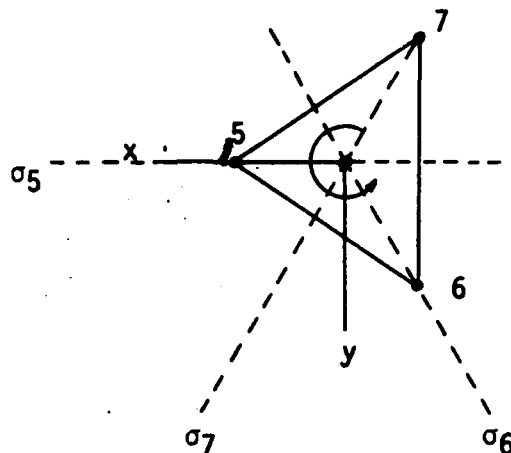
Figure 6. Triangular Axes of Symmetry of C_{3v}

$$C_3 = \begin{pmatrix} \cos 120 & \sin 120 \\ -\sin 120 & \cos 120 \end{pmatrix} = \begin{pmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix}$$

$$C_3^2 = \begin{pmatrix} \cos 240 & \sin 240 \\ -\sin 240 & \cos 240 \end{pmatrix} = \begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix}$$

$$C_3^3 = \varepsilon = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad \sigma_5 \Rightarrow \begin{pmatrix} 5 & 6 & 7 \\ 5 & 7 & 6 \end{pmatrix} \Rightarrow \begin{matrix} x \to x \\ y \to -y \end{matrix}$$

$$\text{or} \quad \sigma_5 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\sigma_6 = \begin{pmatrix} 5 & 6 & 7 \\ 7 & 6 & 5 \end{pmatrix}$$

$$\sigma_6 = \begin{pmatrix} 5 & 6 & 7 \\ 5 & 7 & 6 \end{pmatrix}\begin{pmatrix} 5 & 6 & 7 \\ 7 & 5 & 6 \end{pmatrix} = \begin{pmatrix} 5 & 6 & 7 \\ 7 & 6 & 5 \end{pmatrix}$$

$$\text{or} \quad \sigma_6 = \sigma_5 C_3^2$$

$$\sigma_7 \Rightarrow \begin{pmatrix} 5 & 6 & 7 \\ 6 & 5 & 7 \end{pmatrix} = \begin{pmatrix} 5 & 6 & 7 \\ 5 & 7 & 6 \end{pmatrix}\begin{pmatrix} 5 & 6 & 7 \\ 6 & 7 & 5 \end{pmatrix} = \begin{pmatrix} 5 & 6 & 7 \\ 6 & 5 & 7 \end{pmatrix}$$

$$= \sigma_5 C_3$$

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SUMMARY OF TWO-DIMENSIONAL MATRIX REPRESENTATION OF C_{3v}

$$E = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad\qquad C_3 = \begin{pmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix}$$

$$C_3^2 = \begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix} \qquad \sigma_5 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\sigma_6 = \sigma_5 C_3^2 = \begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & 1/2 \end{pmatrix} \qquad \sigma_7 = \sigma_5 C_3 = \begin{pmatrix} -1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & 1/2 \end{pmatrix}$$

Trace $E = 2$

Trace C_3 = Trace C_3^2 = -1

Trace σ_5 = Trace σ_6 = Trace σ_7 = 0

SECTION XII

RESULTS AND CONCLUSIONS

Application of the theory presented in Sections I-IX of this report, via the computational scheme outlined in Sections X and XI, resulted in a set of self-consistent energy levels for the C_5H_9 cluster which was convergent to at least one part per thousand after 50 iterations. Table 2 lists the occupied and low-lying unoccupied energy levels, and their percent change Δ between the 49th and 50th iterations. The tabulation is arranged according to the corresponding irreducible representations of C_{3v}, namely the two one-dimensional representations A_1 and A_2 (maximum occupancy of two electrons in each level) and the two-dimensional representation E (maximum occupancy of four electrons per level).

Watkins and Messmer (Reference 28) made a calculation similar to ours, but on the cluster C_5H_{12}. They were interested in the properties of diamond in the bulk and, to the extent that their calculation is representative of the solid, ours is representative of the unrelaxed, unreconstructed (111) surface. Comparison of the two calculations is facilitated by making use of the correlation table, Table 3 (Reference 29). This gives the splitting of the levels as the symmetry is lowered from T_d for C_5H_{12} to C_{3v} for C_5H_9. Thus a six-fold degenerate level belonging to the T_1 representation, for example, will split into a two-fold degenerate level belonging to A_2 and a four-fold degenerate level belonging to E.

Table 4 compares the C_5H_{12} valence levels from Figure 2 of Reference 28 with our results for C_5H_9, expressed in eV (1 Ry = 13.606 eV). The comparison is also shown on an energy level diagram in Figure 7.

From Figure 7, it is evident that the cluster corresponding to bulk diamond has a well defined energy gap of 5.56 eV between occupied and empty states. This agrees with the experimental energy gap of 5.4 eV between the top of the valence band and the bottom of the conduction band (Reference 12). For the C_5H_9 cluster, corresponding to the presence

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TABLE 2

ONE-ELECTRON ENERGY LEVELS OF C_5H_9

Level Representation and (Occupancy)	Level Energy, R_y (49th Iteration)	Level Energy, R_y (50th Iteration)	$\Delta(\%)$
1S core of C atom #3. (2)	-20.523	-20.522	0.005
1S core of C atom #4. (2)	-20.698	-20.697	0.005
1S core of C atoms #5, 8 and 9. (6)	-20.675	-20.676	0.005
A1 (2)	-1.92808	-1.92806	0.001
A1 (2)	-1.57929	-1.57857	0.05
A1 (2)	-1.29193	-1.29213	0.02
A1 (2)	-1.18067	-1.18043	0.02
A1 (2)	-0.85135	-0.85174	0.05
A1 (0)	-0.28917	-0.28931	0.05
A1 (0)	-0.15468	-0.15409	0.38
A1 (0)	-0.12237	-0.12269	0.26
A2 (2)	-0.96254	-0.96374	0.12
E (4)	-1.52434	-1.52489	0.04
E (4)	-1.14320	-1.14330	0.01
E (4)	-1.02248	-1.02345	0.09
E (4)	-1.06616	-1.06559	0.06
E (1)	-0.83327	-0.83393	0.08
E (0)	-0.48203	-0.48271	0.14
E (0)	-0.10953	-0.10968	0.15
E (0)	-0.09989	-0.09997	0.08

TABLE 3

CORRELATION TABLE FOR $T_d \rightarrow C_{3v}$

T_d rep.	C_{3v} rep.
A_1	A_1
A_2	A_2
E	E
T_1	$A_2 + E$
T_2	$A_1 + E$

of a free (111) surface, the six-fold degenerate T_2 states at the top of the valence band split away and form a narrow group of partially occupied surface states of width 0.24 eV located in the lower half of the gap. The "Fermi level" in our cluster model, which is at -11.346 eV, lies 1.77 eV from the top of the valence band. These results agree quite well with self-consistent pseudopotential calculations of the diamond (111) surface (Reference 8). The latter obtained a band of partially filled surface states approximately 0.2 eV wide and 1.7 eV above the valence band. They also deduced a value of the work function ϕ of about 7 eV whereas our model predicted $\phi \sim 11$ eV.

In summary, the SCF-Xα scattered-wave method applied to diamond yields results for the electronic structure in the vicinity of the band gap in very good agreement with available experimental data for the band gap in the crystal and with band-structure calculations for the unrelaxed, unreconstructed (111) surface. This suggests that similar cluster models would be useful in studying surface properties such as atomic adsorption as well as bulk properties such as point defects, in other covalently bonded solids having the diamond structure, e.g., Ge, Si and GaAs.

TABLE 4

COMPARISON OF VALENCE LEVELS FOR C_5H_{12} AND C_5H_9

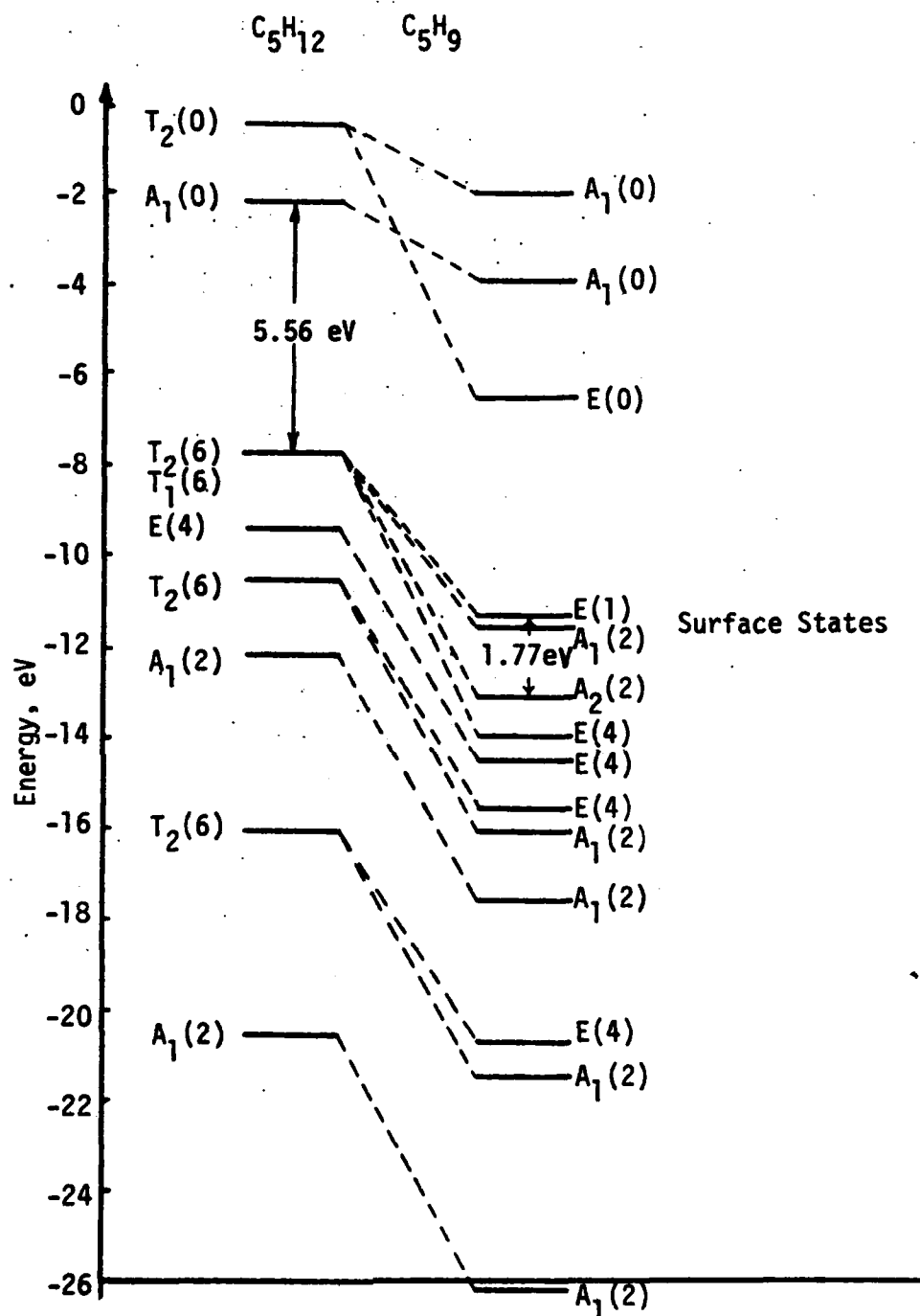| C_5H_{12} levels (eV) and (representation)	C_5H_9 levels (eV) and (representation)
-0.56 (T_2)	-2.097 (A_1)
-2.22 (A_1)	-3.936 (A_1)
	-6.568 (E)
-7.78 (T_2)	-11.346 (E)
	-11.589 (A_1)
-7.78 (T_1)	-13.113 (A_2)
	-13.925 (E)
-9.44 (E)	-14.498 (E)
-10.56 (T_2)	-15.556 (E)
	-16.061 (A_1)
-12.22 (A_1)	-17.581 (A_1)
-16.1 (T_2)	-20.748 (E)
	-21.478 (A_1)
-20.6 (A_1)	-26.233 (A_1)

Figure 7. Valence Energy Level Diagram for C_5H_{12} and C_5H_9
Including Representation and Occupancy

APPENDIX A

$$\text{Proof of the form } G_\ell \sim \frac{\sin(Kr - \frac{\pi\ell}{2} + N_\ell)}{K}$$

Solving Equation 142 by perturbation theory:

$$G_\ell'' + [K^2 - U(r) - \frac{\ell(\ell+1)}{r^2}] \, G_\ell = 0 \tag{A-1}$$

Letting

$G_\ell = g_\ell + \emptyset$ and assume that the product $\emptyset U(r)$ can be neglected,

for small values of $\emptyset$, our perturbation parameter. (A-2)

Substituting Equation 2 into Equation 1 we have

$$g_\ell'' + \emptyset'' + [K^2 g_\ell + K^2\emptyset - Ug_\ell - U\emptyset - \frac{\ell(\ell+1)}{r^2} g_\ell - \frac{\ell(\ell+1)}{r^2} \emptyset] = 0 \tag{A-3}$$

$$g_\ell'' + [K^2 - U(r) - \frac{\ell(\ell+1)}{r^2}] g_\ell + \emptyset'' + [K^2 - \frac{\ell(\ell+1)}{r^2}] \emptyset = 0 \tag{A-4}$$

Looking at part of Equation A-4 which is bounded at the origin

$$\frac{d^2 g_\ell}{dr^2} + [K^2 - \frac{\ell(\ell+1)}{r^2}] g_\ell = 0$$

$$g_\ell \sim \sin(Kr - \frac{1}{2}\ell\pi) \tag{A-5}$$

then we have

$$\frac{d^2\emptyset}{dr^2} + (K^2 - \frac{\ell(\ell+1)}{r^2}) \emptyset = U(r)g_\ell(r) \tag{A-6}$$

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If we let Equation A-7

$$\phi = g_\ell(r) \, N(r) \qquad \text{(A-7)}$$

$$\phi' = g_\ell' N + g_\ell N' \qquad \text{(A-8)}$$

$$\phi'' = g_\ell'' N + 2g_\ell' N' + g_\ell N'' \qquad \text{(A-9)}$$

Substituting Equations A-7 and A-9 into Equation A-6 we have

$$g_\ell'' N + 2g_\ell' N' + g_\ell N'' + (K^2 g_\ell N - \frac{\ell(\ell+1)}{r^2} g_\ell N) = U(r) g_\ell \qquad \text{(A-10)}$$

or

$$N[g_\ell'' + K^2 g_\ell - \frac{\ell(\ell+1)}{r^2} g_\ell] + g_\ell N'' + 2g_\ell' N' = U(r) g_\ell(r) \qquad \text{(A-11)}$$

Substituting Equation A-5 into Equation A-11, we have

$$g_\ell N'' + 2g_\ell' N' = U(r) g_\ell(r) \qquad \text{(A-12)}$$

Multiplying g_ℓ into Equation A-12 we have:

$$\frac{d}{dr} (g_\ell^2 N') = U(r) g_\ell^2(r) \qquad \text{(A-13)}$$

Integrating Equation A-13,

$$g_\ell^2 N' = \int^r U(r) g_\ell^2(r) \, dr \qquad \text{(A-14)}$$

Since N' must be bounded at $r = 0$, and $g_\ell(r)$ behaves like $r^{\ell+1}$ for small r, the lower limit of integration must be zero. Then

$$\frac{dN}{dr} = \frac{1}{[g_\ell(r)]^2} \int_0^\infty U(r) g_\ell^2(r) \, dr \qquad \text{(A-15)}$$

For large r, we have $g_\ell(r) = \sin(Kr - \frac{\pi\ell}{2}]$

or

$$\frac{dN}{dr} \sim \frac{1}{[\sin(Kr - \frac{\pi\ell}{2})]^2} \int_0^\infty U(r)[g_\ell(r)]^2 dr$$

$$= \csc^2(Kr - \frac{\pi\ell}{2}) \int_0^\infty U(r)[g_\ell(r)]^2 dr \qquad (A-16)$$

letting

$$\int_0^\infty U(r)[g_\ell(r)]^2 dr = A_\ell$$

a constant, then

$$\frac{dN}{dr} = \csc^2(Kr - \frac{\pi\ell}{2}) A_\ell \qquad (A-17)$$

Integrating Equation 17

$$N = A_\ell \int \csc^2(Kr - \frac{\pi\ell}{2}) \, dr = -A_\ell \cot(Kr - \frac{\pi\ell}{2}) \qquad (A-18)$$

since

$$\frac{d}{dx}(\cot x) = \frac{d}{dx}\left(\frac{\cos x}{\sin x}\right) = -\frac{\sin x}{\sin x} - \frac{\cos^2 x}{\sin^2 x}$$

$$= -\frac{\sin^2 x - \cos^2 x}{\sin^2 x} = -\csc^2 x$$

$$\Rightarrow \int \csc^2 x = -\cot x$$

then

$$G_\ell = g_\ell + \emptyset = \sin(Kr - \frac{1}{2}\ell\pi) - [\cot(Kr - \frac{\pi\ell}{2}) + \alpha]\frac{A_\ell}{K}$$

$$\times \sin(Kr - \frac{\pi\ell}{2})$$

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or

$$G_\ell = \sin(Kr - \frac{1}{2}\ell\pi) - [\cos(Kr - \frac{\pi\ell}{2}) + \alpha \sin(Kr - \frac{\pi\ell}{2})]\frac{A_\ell}{K}$$

$$= \sin(Kr - \frac{1}{2}\ell\pi)[1 - \frac{\alpha A_\ell}{K}] - \frac{A_\ell}{K}\cos(Kr - \frac{\pi\ell}{2})$$

letting

$$\frac{1 - \frac{\alpha A_\ell}{K}}{\sqrt{(\frac{A_\ell}{K})^2 + [1 - \frac{\alpha A_\ell}{K}]^2}} = \cos N_\ell \quad \text{and} \quad \sin N_\ell = -\frac{A_\ell}{K}$$

$$= \sqrt{(\frac{A_\ell}{K})^2 + [1 - \frac{\alpha A_\ell}{K}]^2} \sin(Kr - \frac{1}{2}\pi + N_\ell)$$

$$= \frac{const}{K}\sin(Kr - \frac{1}{2}\pi + N_\ell)$$

here

$$\sin N_\ell \sim N_\ell = -\frac{A_\ell}{K}$$

where N_ℓ is small.

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APPENDIX B

PROPERTIES OF THE FUNCTIONS $K_\ell^{(1)}(Kr)$ AND $i_\ell(Kr)$

$$\lim_{r\to 0} K_\ell^{(1)}(Kr) = (-1)^\ell \frac{1\cdot 1\cdot 3\cdots(2\ell-1)}{(Kr)^{\ell+1}}$$

$$\lim_{r\to 0} K_\ell^{(1)}(Kr) = (-1)^\ell \frac{\exp(-Kr)}{Kr}$$

$$K_{\ell-1}^{(1)}(Kr) = K_{\ell-1}^{(1)}(Kr) - \frac{2\ell+1}{r} K_\ell^{(1)}(Kr)$$

$$\frac{dK_\ell^{(1)}(Kr)}{d(Kr)} = \frac{1}{2\ell+1}[\ell K_{\ell-1}^{(1)}(Kr) + (\ell+1)K_{\ell-1}^{(t)}(Kr)].$$

$$-K^{(\ell)}(Kr) = K_0^{(1)}(Kr) = \frac{\exp(-Kr)}{Kr}$$

$$K_\ell^{(1)}(Kr) = -\frac{\exp(-Kr)}{Kr}\left(1 + \frac{1}{Kr}\right)$$

$$K_2^{(1)}(Kr) = -\frac{\exp(-Kr)}{Kr}\left[1 + \frac{3}{Kr} + \frac{3}{(Kr)^2}\right]$$

$$K_3^{(1)}(Kr) = -\frac{\exp(-Kr)}{Kr}\left[1 + \frac{6}{Kr} + \frac{15}{(Kr)^2} + \frac{15}{(Kr)^3}\right]$$

$$K_2^{(1)}(Kr) = \frac{\exp(-Kr)}{Kr}\left[1 + \frac{10}{Kr} + \frac{45}{(Kr)^2} + \frac{105}{(Kr)^3} + \frac{105}{(Kr)^4}\right]$$

$$\lim_{r\to 0} i_\ell(Kr) = \frac{(Kr)^\ell}{1\cdot 3\cdot 5\cdots(2\ell+1)}$$

$$\lim_{r\to 0} i_\ell(Kr) = \frac{\exp(Kr)}{Kr}$$

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$$i_\ell(Kr) = \frac{(Kr)^\ell}{1 \cdot 3 \cdot 5 \cdots (2\ell+1)} \left[1 + \frac{(Kr)^2}{2(2\ell+3)} + \frac{(Kr)^4}{2 \cdot 4 \cdot (2\ell+3)(2\ell+5)} + \cdots \right]$$

$$\frac{di_\ell(Kr)}{d(Kr)} = \frac{1}{2\ell+1} \left[\ell i_{\ell-1}(Kr) + (\ell+1)(i_{\ell+1}(Kr) \right]$$

$$i_\ell(Kr) \frac{dK_\ell^{(1)}(Kr)}{d(Kr)} - K_\ell^{(1)}(Kr) \frac{di_\ell(Kr)}{d(Kr)} = \frac{(-1)^{\ell-1}}{Kr^2}$$

APPENDIX C

THE DERIVATION OF THE INTEGRAL SCHRÖDINGER EQUATION

The Schrödinger integral equation is derived as follows:

$$\frac{-\hbar^2}{2m} \nabla^2 \psi_{(\underline{r})} - \epsilon\, \psi_{(\underline{r})} + U(\underline{r})\, \psi_{(\underline{r})} = 0 \qquad (C-1)$$

or

$$(\nabla^2 + K^2)\psi = V\psi \qquad (C-2)$$

where

$$K^2 = \frac{2\mu E}{\hbar^2} \text{ and } V = 2\mu\, \frac{U}{\hbar^2}$$

for a particular solution of Equation C-2 is constructed in terms of the Green's function $G(r,r')$ which is the solution of the equation

$$(\nabla^2 + K^2)G(\underline{r},\ \underline{r}') = -4\pi\delta\ (\underline{r} - \underline{r}').$$

The expression $- \frac{1}{4\pi} \int G\ (\underline{r},\ \underline{r}')\ V(\underline{r}')\ \psi(\underline{r}')\ d^3r'$ solves Equation C-2 since $(\nabla^2 + K^2)\psi = V\psi$. Multiplying both sides by $G(\underline{r},\ \underline{r}')$ and integrating: $\int dr'\ G(\nabla^2 + K^2)\psi = \int VG\ \psi dr'$ since $\int d\underline{r}'\ G\nabla^2\psi = \int \psi\nabla^2 G\ d\underline{r}',\ \int d\underline{r}'\ [\psi\nabla^2 G + K^2 G\psi] = \int VG\ \psi dr' = \int d\underline{r}'\ \psi[\nabla^2 G + K^2 G] = -4\pi \int d\underline{r}'\ \psi_{(r,r')}\delta(\underline{r} - \underline{r}') = \psi(\underline{r})(-4\pi)$ $\therefore\ \psi(\underline{r}) = - \frac{1}{4\pi} \int V(\underline{r}')G(\underline{r},\ \underline{r}')\ \psi(\underline{r}')\ d\underline{r}'$; letting $\frac{G(\underline{r},\ \underline{r}')}{-4\pi} = G_0(\underline{r},\ \underline{r}')$, then $\psi(\underline{r}) = \int V(\underline{r}')\ G_0(\underline{r},\ \underline{r}')\ \psi(\underline{r}')\ d\underline{r}'$ as was to be proved.

APPENDIX D

INTEGRAL REPRESENTATION OF THE FREE-SPACE GREEN'S FUNCTION

Consider applying the Fourier transformation to the equation

$$(\nabla^2 + e) \, G(\underline{r} - \underline{r}') = -4\pi \, \delta(\underline{r} - \underline{r}')$$

If we introduce $G(\underline{r} - \underline{r}') = \int g(K') \, e^{iK'_j \cdot (\underline{r} - \underline{r}')} d^3\underline{K}'$

and $\delta(\underline{r} - \underline{r}') = \frac{1}{(2\pi)^3} \int e^{iK' \cdot (\underline{r} - \underline{r}')} d^3K'$, then substituting

these expressions we have:

$$\int (\nabla^2 + e) \, g(K') \, e^{iK' \cdot (\underline{r} - \underline{r}')} d^3_{K'} = \frac{-4\pi}{(2\pi)^3} \int e^{iK' \cdot (\underline{r} - \underline{r}')} d^3K'$$

$$= \int g(K') \, [-K'^2 + e] \, e^{iK' \cdot (\underline{r} - \underline{r}')} d^3K' = \frac{1}{2\pi^2} \int e^{iK' \cdot \underline{r} - \underline{r}'} d^3K'$$

$$\therefore \, g(\underline{K}') = [-K'^2 + e]^{-1} \cdot \frac{-1}{2\pi^2} \quad \text{hence}$$

$$G(\underline{r} - \underline{r}') = \int g(K') \, e^{iK' \cdot (\underline{r} - \underline{r}')} d^3K'$$

$$= \frac{-1}{2\pi^2} \int \frac{e^{i\underline{K}' \cdot \underline{r} - \underline{r}'}}{[e - K'^2]} d^3K'$$

Since $G_0(\underline{r} - \underline{r}') = \frac{G(\underline{r} - \underline{r}')}{-4\pi}$, then

$$G_0(\underline{r} - \underline{r}') = \frac{1}{(2\pi)^3} \int \frac{e^{i\underline{K}' \cdot (\underline{r} - \underline{r}')}}{[e - K'^2]} dK'$$

or

$$= \frac{1}{(2\pi)^3} \int \frac{dK e^{i\underline{K}\cdot(\underline{r} - \underline{r}')}}{[e - K^2]} = G_0(\underline{r} - \underline{r}') = G_0(\underline{r}, \underline{r}', e)$$

APPENDIX E

DERIVATION OF AN ALTERNATE FORM OF GREEN'S FUNCTION

The free-space Green's function was derived in Appendix D. It is:

$$G_0(r_\alpha, r'_\beta ; e) = \frac{1}{(2\pi)^3} \int \frac{d\underline{q}\, \exp[i\underline{q} \cdot (\underline{r}_\alpha - \underline{r}'_\beta - \underline{R}_{\alpha\beta}]}{e - q^2}$$

where $\underline{R}_{\alpha\beta} \equiv \underline{R}_\beta - \underline{R}_\alpha$.

For the case where $\beta = \alpha$, the alternative partial wave

expansion is given by

$$G_0(\underline{r}, \underline{r}'; e) = - \frac{1}{4\pi} \frac{\exp(-K|\underline{r} - \underline{r}'|)}{|\underline{r} - \underline{r}'|}$$

This form is used profusely and therefore merits a
derivation.

Let us consider the momentum integral $(\vec{q} \equiv \vec{p})$ representa-
tion:

$$I = \int \frac{e^{i\underline{q} \cdot \underline{r}}}{K^2 - q^2}\, d\underline{q} \quad \text{where} \quad e = K^2 \text{ and } K \text{ is a complex number}$$

with $\mathrm{re}K > 0$. We then have

$$I = \int_0^\infty \int_0^{2\pi} \int_0^\pi \frac{e^{iqr\cos\theta}}{K^2 - q^2} q^2 \sin\theta \, d\theta \, d\phi \, dq.$$

Looking at the integral: $\int_0^\pi \frac{e^{iqr\cos\theta}}{K^2-q^2} \sin\theta \, d\theta$ we see

that it is just $= -\frac{e^{iqr\cos\theta}}{iqr(K^2-q^2)} \Big|_0^\pi = \frac{2\sin qr}{qr(K^2-q^2)}$

$$\therefore \quad I = \frac{4\pi}{r} \int_0^\infty \frac{q\sin qr}{(K^2-q^2)} \, dq$$

$$= \frac{2\pi}{ir} \int_0^\infty \frac{q(e^{iqr} - e^{-iqr})}{K^2 - q^2} \, dq = -\frac{2\pi i}{r} \int_{-\infty}^\infty \frac{qe^{iqr}}{K^2 - q^2} \, dq$$

where $-\infty < q < 0$. The integral $-\frac{2\pi i}{r} \int_{-\infty}^\infty \frac{qe^{iqr}}{K^2-q^2} \, dq$ is the principal

part of the contour integral $-\frac{2\pi i}{r} \oint \frac{qe^{iqr}}{K^2-q^2} \, dq$ in the complex q

plane.

Here the integration is taken over the infinite semicircle
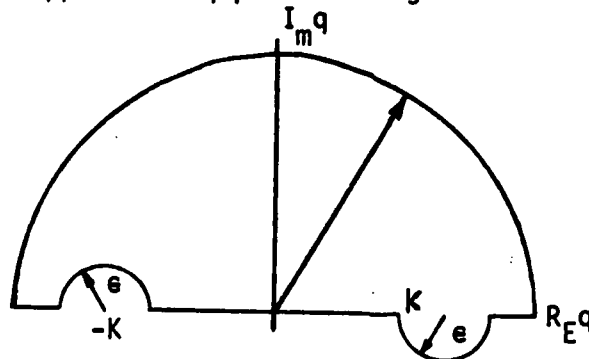in the upper half-q plane in Figure E-1.

Figure E-1. Contour Used for Evaluating the Green's Function
for Case (a)

The contour integral is equal to $2\pi i$ times the sum of the residues of the poles of the integrand which lie within the contour. Hence we have

Case(a)   im $K > 0$ - pole at $q = K$

$$2\pi i\sigma \quad \text{for} \quad \frac{2\pi i}{r} \oint \frac{qe^{iqr}}{(K-q)(K+q)}$$

$$= 2\pi i \lim_{q \to K} \frac{2\pi i}{r} \frac{(q)e^{iqr}}{(K-q)(K+q)} (K-q)$$

$$= (2\pi i) \frac{2\pi i}{r} \frac{K e^{iKr}}{2K}$$

$$= - 2\pi^2 \frac{e^{iKr}}{r}$$

Therefore, the more general vector representation

$$I = \int \frac{e^{iq\cdot(r - r')}}{K^2 - q^2} \, dq \quad \text{becomes}$$

$$- 2\pi^2 \frac{e^{iK|r - r'|}}{|r - r'|}.$$

Similarly, Case (b),

im $K < 0$ - pole at $q = -K$ with contour of Figure E-2,

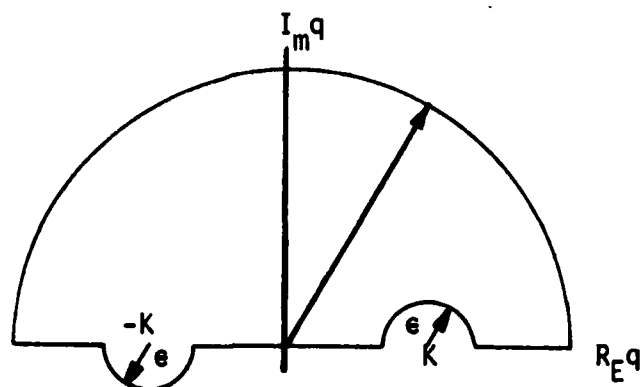gives $\int \frac{e^{iq\cdot r}}{K^2-q^2} \, dq \to -2\pi^2 \frac{e^{-iKr}}{r}$

Figure E-2. Contour Used for Evaluating the Green's Function
for Case (b)

Therefore the more general vector representation

$$I = \int \frac{e^{i\underline{q}\cdot(\underline{r} - \underline{r}')}}{K^2 - q^2} \, d\underline{q} \quad \text{becomes} \quad -2\pi^2 \frac{e^{-iK|r - r'|}}{|r - r'|}$$

Then $\qquad G_0(r_\alpha, r'_\beta ; e) = \frac{-2\pi^2}{(2\pi)^3} \frac{e^{iK|\underline{r}-\underline{r}'|}}{|\underline{r} - \underline{r}'|} = -\frac{1}{4\pi} \frac{e^{iK|\underline{r} - \underline{r}'|}}{|\underline{r} - \underline{r}'|}$

as was to be proven.

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APPENDIX F

DERIVATION OF ASYMPTOTIC FORMS FOR HANKEL AND BESSEL FUNCTIONS OF REAL ARGUMENT

Consider the equation $(\nabla^2 + K_0^2)\psi(\underline{r}) = S(\underline{r})$, where ∇^2 is the spherical coordinates Laplacian.

A solution exists when one finds the Green's function

$$G(\underline{r}, \underline{r}') = (\nabla^2 + K_0^2)^{-1} \delta(\underline{r} - \underline{r}') \qquad \text{(F-1)}$$

and then uses

$$\psi(\underline{r}) = \int G(\underline{r}, \underline{r}') S(\underline{r}') \, d\underline{r}' \qquad \text{(F-2)}$$

Since K_0^2 is complex in general and the eigenvalues of ∇^2 are real, the operator $(\nabla^2 + K_0^2)$ cannot have a zero eigenvalue. Hence, the existence of the Green's function G is a possibility.

In order to solve this expression and determine the form for the Green's function, some preliminary results have to be obtained We know that $\delta(\underline{r} - \underline{r}') = (\frac{1}{2\pi})^3 \int e^{i\underline{K} \cdot (\underline{r} - \underline{r}')} \, d\underline{K}$ that is:

$$\delta(x-x') \, \delta(y-y') \, \delta(z-z') \qquad \text{(F-3)}$$

$$= \frac{1}{(2\pi)^3} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} e^{i[K_x(x-x') + K_y(y-y') + K_z(z-z')]}$$

$$dK_x dK_y dK_z$$

Transforming to spherical coordinates, we have (see Appendix G)

$$\delta(\underline{r} - \underline{r}') = \frac{\delta(r-r')\delta(\theta-\theta')\delta(\phi-\phi')}{r^2 \sin\theta}$$

Thus

$$\frac{\delta(r-r')}{r^2} \frac{\delta(\theta-\theta')}{\sin} \delta(\phi-\phi') = \frac{1}{(2\pi)^3} \int_0^{2\pi} \int_0^\pi \int_0^\infty$$

$$e^{i\underline{K}\cdot(\underline{r}-\underline{r}')} K^2 \sin\alpha\, dK\, d\alpha\, d\beta$$

(F-4)

The expansion of a plane wave $e^{i\underline{K}\cdot\underline{r}}$, traveling in an arbitrary direction α,β (i.e. $\underline{K}$ has components $K_x = K \sin\alpha\cos\beta$; $K_y = K \sin\alpha\sin\beta$, $K_z = K \cos\alpha$) is

$$e^{i\underline{K}\cdot\underline{r}} = 4\pi \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{+\ell} i^\ell j_\ell(Kr)\, \bar{Y}_\ell^m(\alpha,\beta)\, Y_\ell^m(\theta,\phi)$$

(F-5)

Substituting Equation F-5 into Equation F-4 for $e^{i\underline{K}\cdot\underline{r}}$ and the complex conjugate of Equation F-5 for $e^{i k \cdot r'}$ into Equation F-4, we have:

$$\frac{\delta(r-r')}{r^2} \frac{\delta(\theta-\theta')}{\sin} \delta(\phi-\phi')$$

$$= \left(\frac{1}{2\pi}\right)^3 \int_0^{2\pi}\int_0^\pi\int_0^\infty 4\pi \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{+\ell} i^\ell j_\ell(Kr)\bar{Y}_\ell^m(\alpha,\beta)$$

$$\times Y_\ell^m(\theta,\phi) \cdot 4\pi \sum_{L=0}^{\infty} \sum_{M=-L}^{+L} (-i)^L j_L(Kr')Y_L^M(\theta,\phi)\bar{Y}_L^M(\theta',\phi')$$

$$\times K^2 \sin\alpha\, d\alpha\, d\beta\, dK$$

(F-6)

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or in vector form

$$\delta(\underline{r} - \underline{r}') = \frac{2}{\pi} \sum_{\ell,m} \sum_{L,M} [i^{\ell}(-i)^{L} \, \overline{Y}_{L}^{M}(\theta',\phi') \, Y_{\ell}^{m}(\theta,\phi) \tag{F-7}$$

$$\times \int_{0}^{\infty} j_{\ell}(Kr) \, j_{L}(Kr') \, K^{2}dK \int_{0}^{2\pi}\int_{0}^{\pi} Y_{\ell}^{m}(\alpha,\beta) Y_{L}^{M}(\alpha,\beta) \, \sin\alpha \, d\alpha \, d\beta.$$

Because of the orthonormality condition:

$$\int_{0}^{2\pi}\int_{0}^{\pi} Y_{\ell}^{m}(\alpha,\beta) \, Y_{L}^{M}(\alpha,\beta) \, \sin\alpha \, d\alpha \, d\beta = \delta_{\ell L} \, \delta_{mM} \tag{F-8}$$

Therefore,

$$\delta(\underline{r} - \underline{r}') = \frac{2}{\pi} \sum_{\ell,m} \overline{Y}_{\ell}^{m}(\theta',\phi') \, Y_{\ell}^{m}(\theta,\phi) \int_{0}^{\infty} j_{\ell}(Kr) \, j_{\ell}(Kr') K^{2}dK \tag{F-9}$$

looking back at Equation F-1, namely: $G(\underline{r}, \underline{r}') = (\nabla^{2} + K_{0}^{2})^{-1}$

$\delta(\underline{r} - \underline{r}')$ we see that the Green's function will have an expansion

in terms of spherical harmonics and Bessel functions. Therefore

we can let

$$G(\underline{r}, \underline{r}') = \sum_{\ell,m} g_{\ell}(\underline{r}, \underline{r}') \, Y_{\ell}^{m}(\theta',\phi') \, Y^{m}(\theta,\phi) \tag{F-10}$$

It is necessary to address the problem of determining the reciprocal of the operator $\nabla^{2} + K_{0}^{2}$. To do this let us consider the

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operator $-\alpha^2\nabla^2 + 1$ in spherical coordinates, and the inhomogeneous partial differential equation,

$$Lf(\underline{r}) \equiv (\nabla^2 + K_0^2)\, f(\underline{r}) = s(\underline{r}) \tag{F-11}$$

where $\underline{r}$ denotes the vector with components $r\sin\phi\cos e$, $r\sin\phi\sin\phi$ and $r\cos\phi$ and

$$\nabla^2 \equiv \frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \tag{F-12}$$

Now, $g(\underline{r}, \underline{r}') = L^{-1}\delta(\underline{r} - \underline{r}')$,
gives

$$G(r, r') = L^{-1} \frac{2}{\pi}\sum_{\ell,m}\overline{Y}_\ell^m(\theta',\phi')\,Y_\ell^m(\theta,\phi)\int_0^\infty j_\ell(Kr)j_\ell(Kr')K^2 dK$$

$$= \frac{2}{\pi}\sum_{\ell,m}\overline{Y}_\ell^m(\theta',\phi')\,Y_\ell^m(\theta,\phi)\int_0^\infty \frac{j_\ell(Kr)\,j_\ell(Kr')}{K_0^2 - K^2}K^2 dK \tag{F-13}$$

where the form of the denominator can be seen from Appendix D.

Comparing Equations F-10 and F-13 we have

$$g_\ell(r, r') = \frac{2}{\pi}\int_0^\infty \frac{j_\ell(Kr)j_\ell(Kr')K^2 dK}{K_0^2 - K^2} \tag{F-14}$$

Since $g_\ell(r, r')$ is even function in K, the integral can be re-written as

$$g_\ell(r, r') = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{j_\ell(Kr)j_\ell(Kr') \ K^2 dK}{K_0^2 - K^2} \qquad \text{(F-15)}$$

where the limits have been changed from $0 \le K < \infty$ to $-\infty < K < \infty$.

We can write in partial fractions:

$$\frac{K^2}{K_0^2 - K^2} = \frac{A}{K_0 + K} + \frac{B}{K_0 - K}$$

Thus

$$K^2 = A(K_0 - K) + B(K_0 + K). \quad \text{For } K_0 = K, \ K^2 = 2Bk, \text{ and}$$

$B = \frac{K}{2}$. For $K_0 = -K$, $K^2 = -2KA$ and $A = -\frac{K}{2}$ $\therefore$.

$$\frac{K^2}{K_0^2 - K^2} = \frac{-K/2}{K_0 + K} + \frac{K/2}{K_0 - K} = \frac{-K}{2} \left[\frac{1}{K - K_0} + \frac{1}{K + K_0} \right] \qquad \text{(F-16)}$$

Now

$$\frac{K}{K + K_0} + \frac{K}{K - K_0} = \frac{2K}{K - K_0} + \left(\frac{K}{K + K_0} - \frac{K}{K - K_0} \right) \qquad \text{(F-17)}$$

Since the term in parentheses on the right is an odd function in K, it will make no contribution to the integral. Therefore,

$$g_\ell(r, r') = -\frac{1}{\pi} \int_{-\infty}^{\infty} j_\ell(Kr)j_\ell(Kr') \frac{K}{K - K_0} dK \qquad \text{(F-18)}$$

We shall integrate Equation F-18 by the use of contour integration. Since $j_\ell(x) = \frac{1}{2} [h_\ell^{(1)}(x) + h_\ell^{(2)}(x)]$ and $h_\ell^{(1)}(x) \sim \frac{e^{ix}}{x}$; $h_\ell^{(2)}(x) \sim \frac{e^{-ix}}{x}$ for $x \to \infty$, the integral will consist of terms

behaving like $e^{\pm iKr}$ and $e^{\pm iKr'}$. For the case $r > r'$

$$g_\ell(r,r') = -\frac{1}{\pi} \int_{-\infty}^{\infty} \frac{1}{4} \left(e^{\frac{iKr + e^{-iKr}}{Kr}} \right) \left(e^{\frac{iKr' + e^{-iKr'}}{Kr'}} \right) \left(\frac{K}{K-K_0} \right) dK$$

$$= -\frac{1}{2\pi} \int_{-\infty}^{\infty} \left(e^{\frac{iKr + e^{-iKr}}{Kr}} \right) \frac{K}{K-K_0} j_\ell(Kr') \, dK$$

Then the two parts of the term $j_\ell(Kr)$ determine how the contours are to be closed. The $h_\ell^{(1)}(Kr)$ part of $j_\ell(Kr)$ gives a contribution at $K = K_0$ when the contour is closed around the upper half-plane. Since the $h_\ell^{(2)}(Kr)$ part causes the contour to be closed around the lower half plane, where no pole is included, it gives zero contribution.

$$\therefore \, g_\ell(r, r') = \frac{-2\pi i}{2\pi} j_\ell(K_0 r') h_\ell^{(1)}(K_0 r) \text{ for } r > r'$$

$$= -i j_\ell(K_0 r') h_\ell^{(1)}(K_0 r)$$

A similar calculation in the case where $r < r'$ yields

$$g_\ell(r, r') = -i K_0 h_\ell^{(1)}(K_0 r') j_\ell(K_0 r) \quad r < r'$$

We now give the details of the contour integration. We can write

$$j_\ell(Kr) = \frac{1}{2} (h_\ell^{(1)}(Kr) + h_\ell^{(2)}(Kr)) = \frac{1}{2} \left(\frac{e^{iKr}}{Kr} + \frac{e^{-iKr}}{Kr} \right)$$

$$\therefore g(r, r') = \frac{-1}{2\pi} \int_{-\infty}^{\infty} \frac{e^{iKr} j_\ell(Kr')dK}{(K-K_0)r}$$

$$(I_1)$$

$$- \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{e^{-iKr} j_\ell(Kr')dK}{r(K-K_0)}$$

$$(I_2)$$

Call these two terms $-I_1$ and $-I_2$ respectively: $q_\ell(r,r') = -I_1 - I_2$.

Looking at integral I_1, we seek the solution to $\frac{1}{r} \oint_C \frac{e^{iZ} j_\ell(\frac{zr'}{r})dz}{z-z_0}$

where $Z = Kr$; $Z_0 = K_0 r$; let $\frac{r'}{r} = \alpha$. Then we have $\frac{1}{r} \oint_C \frac{e^{iZ} j_\ell(\alpha z)dz}{z-z_0}$.
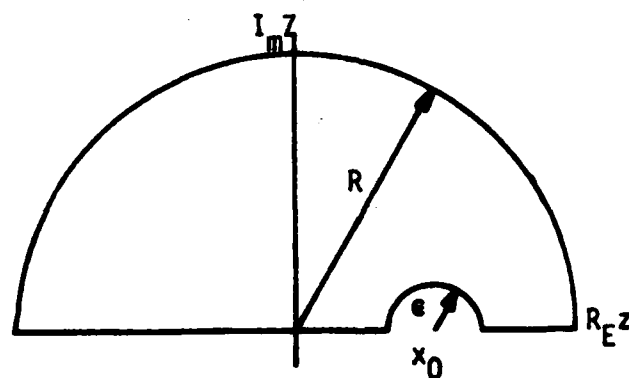
Consider the contour shown in Figure F-1.

Figure F-1. Contour for Evaluation of g (r,r')

Integration around this contour gives

$$0 = \oint \frac{e^{iz}j_\ell(\alpha z)dz}{z - z_0} = \int_{-R}^{x_0 - e} \frac{e^{ix}j_\ell(\alpha x)dx}{x - x_0}$$

$$+ \int_\pi^0 \frac{e^{i(x_0 + ee^{i\theta})}j_\ell(\alpha [x_0 + ee^{i\theta}])iee^{i\theta}d\theta}{(x_0 + ee^{i\theta}) - x_0}$$

$$+ \int_{x_0 + e}^R \frac{e^{i(x + e)}j_\ell(\alpha[x_0 + e])dx}{(x + e) - x_0}$$

$$+ \int_R^{-R} \frac{e^{iRe^{i\theta}}j_\ell[\alpha Re^{i\theta}]iR_e^{i\theta}d\theta}{Re^{i\theta} - z_0}$$

Taking the limits as $R \to \infty$ and $e \to 0$, we see that the *first* and third integrals combine to give the integral $\int_{-\infty}^{\infty} \frac{e^{ix}j_\ell[\alpha x]dx}{x - x_0}$.

The second integral is:

$$\lim_{e \to 0} \int_\pi^0 \frac{e^{i(x_0 - ee^{i\theta})}j_\ell[\alpha(x_0 + ee^{i\theta})]iee^{i\phi}d\theta}{(x_0 + ee^{i\theta}) - x_0}$$

$$= -\pi i e^{ix_0} j_\ell(\alpha x_0)$$

and the fourth integral is

$$\lim_{R\to\infty}\int_{-R}^{R}\frac{\ell^{iR^{\ell i\theta}}j_{\ell}[\alpha Re^{i\theta}]\,iR\epsilon^{i\theta}d\theta}{Re^{i\theta}-z_0}$$

$$\lim_{R\to\infty}\int_{-R}^{R}ie^{iR\cos\theta}e^{-R\sin\theta}j_{\ell}[\alpha R\ell^{i\theta}]\,d\theta\to 0$$

since $j_{\ell}[\alpha R\ell^{i\theta}]$ is a bounded function.

$$\therefore \oint\frac{e^{iz}j_{\ell}[\alpha z]dz}{z-z_0}=0=-\pi i\epsilon^{ix_0}j_{\ell}(\alpha x_0)$$

$$+\int_{-\infty}^{\infty}\frac{e^{ix}j_{\ell}[\alpha x]\,dx}{x-x_0}$$

$$\therefore \int_{-\infty}^{\infty}\frac{e^{ix}j_{\ell}[\alpha x]\,dx}{x-x_0}=+\pi i\epsilon^{ix_0}j_{\ell}(\alpha x_0)$$

changing variables back from z to K gives $+ie^{iK_0 r}j_{\ell}(K_0 r')$ for the value of this integral.

For I_2, we can change sign, letting $-Kr = z$ to give the integral

$$\frac{-1}{2\pi r}\int_{+\infty}^{-\infty}\frac{e^{ix}j_{\ell}(-\frac{x}{r}r')(-dx)}{(K-K_0)}$$

$$= \frac{-1}{2\pi r} \int_{-\infty}^{\infty} \frac{e^{ix} j_\ell (-\frac{x}{r} r') dx}{-x - x_0}$$

$$= \frac{1}{2\pi r} \int_{-\infty}^{\infty} \frac{e^{ix} j_\ell (-\frac{x}{r} r') dx}{x + x_0}$$

Since the pole $x = -x_0$ does not exist on the aforementioned contour, then integral $I_2 = 0$.

$$\therefore \; I_1 = -\int_{-\infty}^{\infty} \frac{e^{ix} j_\ell [dx] dx}{x - x_0} = -\pi i e^{ix_0} J_\ell(\alpha x_0) = -\pi i h_\ell^{(1)}(x_0) J_\ell(\alpha x_0)$$

APPENDIX G

COORDINATE TRANSFORMATION OF DIRAC'S DELTA FUNCTIONS

A locally integrable function $f(x) = f(x_1,\ldots,x_n)$ defines a distribution through $\langle f, \emptyset \rangle = \int_{R_n} f(x)\,\emptyset(x)\,dx$.

It is useful to change coordinate systems at times. To show how this is done, we let $U_1,\ldots,U_n$ be new coordinates that can be obtained from $x_1,\ldots,x_n$ by the transformation law $U = U(x)$, that is, $U_1(x_1,\ldots,x_n),\ldots,U_n = U_n(x_1,\ldots,x_n)$. If the Jacobian J of x with respect to u is <u>positive</u> everywhere

$$\langle f, \emptyset \rangle = \int_{R_n} f(x)\,\emptyset(x)\,dx \qquad\qquad (G\text{-}1)$$

$$= \int_{u\text{ space}} f(x(U))\,\emptyset(x(u))\,J\,du = \int_{u\text{-space}} \tilde{f}(u)J\tilde{\emptyset}(u)\,du$$

where $\tilde{\emptyset} \equiv \emptyset(x(u))$; $\tilde{f}(u) \equiv f(x(u))$.

Equation G-1 can be used to interpret coordinate changes for arbitrary distributions. Considering $f = \delta(x-x') = \delta(x_1-x')\ldots\delta(x_n-x'_n)$, then $\langle f, \phi \rangle = \phi(x') = \phi(u')$, where $u' = u(x')$. Thus, for Equation G-1 to be consistent, we need

$$\tilde{f}(u)J = \delta(U_1-U'_1)\,\ldots\,\delta(U_n-U'_n)$$

or since

$$\tilde{f}(u) = \delta[x(u)-x']$$

we find

$$\delta(x-x') = \frac{\delta(U_1-U'_1)\,\ldots\,\delta(U_n-U'_n)}{J} \qquad\qquad (G\text{-}2)$$

If we only know that $J \geq 0$, Equation G-2 can still be use, that is, if J does not vanish at U', because only the value of J at u' affects the right side of Equation G-2.

To calculate the transformation of the delta function from x-space to spherical space, we are required to calculate the Jacobian for $\delta(r-r')$, $\delta(\theta-\theta')$ and $\delta(\phi-\phi')$; $x = r \sin\theta \cos\phi$, $y = r \sin\theta \sin\phi$ and $z = r \cos\theta$.

$$J = \frac{\partial(x,y,z)}{\partial(r,\theta,\phi)} = \begin{vmatrix} \frac{\partial x}{\partial r} & \frac{\partial x}{\partial \theta} & \frac{\partial x}{\partial \phi} \\ \frac{\partial y}{\partial r} & \frac{\partial y}{\partial \theta} & \frac{\partial y}{\partial \phi} \\ \frac{\partial z}{\partial r} & \frac{\partial z}{\partial \theta} & \frac{\partial z}{\partial \phi} \end{vmatrix}$$

$$= \begin{vmatrix} \sin\theta \cos\phi & r \cos\theta \cos\phi & -r\sin\theta \sin\phi \\ \sin\theta \sin\phi & r \cos\theta \sin\phi & r\sin\theta \cos\phi \\ \cos\theta & -r \sin\theta & 0 \end{vmatrix}$$

$$= r^2\cos^2\theta \sin\theta \cos^2\phi + r^2 \sin^3\theta \sin^2\phi$$

$$+ r^2 \sin\theta \cos^2\theta \sin^2\phi + r^2 \sin^3\theta \cos^2\phi$$

$$= r^2 \cos^2\theta \sin\theta + r^2 \sin^3\theta = r^2 \sin\theta$$

$$\therefore J = r^2 \sin\theta$$

$$\delta(x-x') = \frac{\delta(r-r') \, \delta(\theta-\theta') \, \delta(\phi-\phi')}{r^2 \sin\theta}$$

APPENDIX H

SECULAR DETERMINANT AND EIGENVALUES

To find energy eigenvalues for a state, the matrix elements are constructed and the determinant is examined as a function of the energy to find the zeros. A typical plot of the secular determinant for crystalline zirconium is shown in Figure H-1. The roots are found either graphically or by interpolation schemes.

The determinant of a large matrix is evaluated by a sweep-out procedure which results in a matrix with only zeros on one side of the main diagonal. The determinant for this kind of matrix is simply the product of the diagonal elements. The procedure, used in our energy program, can best be illustrated by an example.

Given the matrix

$$M^{ij} = \begin{pmatrix} 2 & 4 & 6 \\ 4 & 6 & 16 \\ 6 & 16 & 32 \end{pmatrix}$$

we add (-2) times each of the elements of row 1 to the corresponding elements in row 2. Similarly we add (-3) times row 1 to the third row.

The result is

$$\begin{pmatrix} 2 & 4 & 6 \\ 0 & -2 & 4 \\ 0 & 4 & 14 \end{pmatrix}$$

which has zeros under the first diagonal element. The same procedure is applied to the second diagonal element. We add (+2) times the elements in row 3 to get

$$\begin{pmatrix} 2 & 4 & 6 \\ 0 & -2 & 4 \\ 0 & 0 & 22 \end{pmatrix} = m^{ij}$$

the determinant (2) (-2) (22) = -88.

The operations on a particular matrix element which result from applying this sweep-out procedure to the entire matrix are given by

$$m^{ij} = M^{ij} - \sum_{u=1}^{I-1} m^{iu} m^{uj} / m^{uu}$$

where I is the smaller of i or j. M^{ij} is the original matrix element and m^{ij} is the corresponding matrix element after the sweep-out procedure.
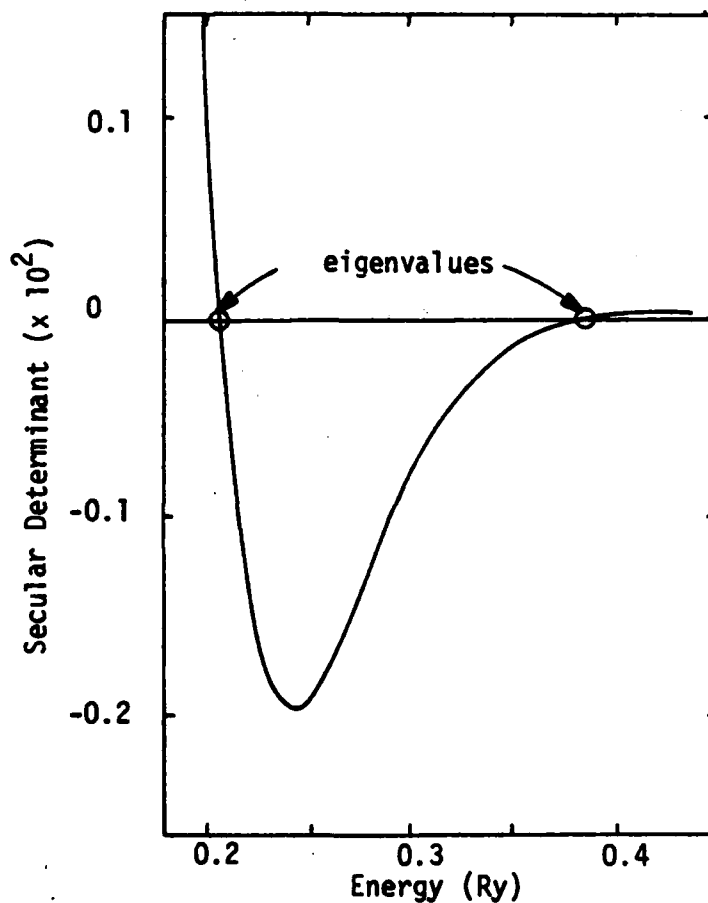

Figure H-1. Secular Determinant as a Function of Energy for Zirconium at the Symmetry Point Γ

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